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1924

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TABLE OF CONTENTS

Volume 16, Part 1

		PAGE
Filtration in the Beet Sugar Industry	Joseph Maudru,	1
The Hot Saccharate Process of the Beet Sugar Industry	R. W. Shafor,	19
The Barium Process of De-Sugarizing Beet Molasses	H. W. Dahlberg,	35
Disposal of Waste From Beet Sugar Industry	Edward Bartow,	47
Technical Accounting in the Sugar Industry	H. E. Zitkowski,	55
Some Factors and Principles Involved in the Separation and Collection of Dust, Mist and Fume from Gases	Evald Anderson,	69
Heat Transfer in Steam-Jacketed Evaporators	H. L. Olin, M. H. Dowell and C. M. Toynbee,	87
Tyler Electric Silica Still	J. C. Olsen, W. Lindenthal and I. Sherman,	101
Concentrating Dilute Nitric Acid	Clifford D. Carpenter and Joseph A. Babor,	111
Chemical Engineering Aspects of Water Treatment for Railroads	William M. Barr,	149
Refined Sulphurs: Their Manufacture and Uses	Charles A. Newhall,	163
Progress in the Application of Continuous Hydrometallurgical Methods in the Chemical Industry	John V. N. Dorr,	185
Treatment of Industrial Wastes to Prevent Stream Pollution	Frank Bachmann and E. B. Besselievre,	203
Index		211

TRANSACTIONS OF THE AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

FILTRATION IN THE BEET SUGAR INDUSTRY

By JOSEPH MAUDRU

Read and discussed at the Denver Meeting, July 15, 1924

Beet Sugar is separated from liquors which have been partly freed of the non-sugars with which it is grown, by crystallization. The raw part of the process is largely concerned with the separation of the impure sugar juices from the plant structure and with the purification of these juices to the highest point possible. The finishing part of the process is concerned with the exhaustion, by crystallization, of the mother liquors to as low a degree as possible. The attainable spread between the highest point to which the juices can be purified on the one hand and the lowest attainable point to which the final syrups can be exhausted on the other hand, is a measure of the performance of the total operation. With this view in mind, Filtration as a specific means of purification is a very important subject. In a single process factory, i.e., one with no process for the recovery of sugar from final molasses, the juices and syrups are subjected to no less than six successive filtrations. After each operation on the juices, such as carbonation, sulphitation, concentration, etc., comes a filtration. These filtrations may be conveniently divided into two classes:

a. The separation of quantity suspension.
b. Clarification or the removal of very light suspensions.

In this paper we shall consider only that part dealing with the separation of solids which occur in generous amounts. Probably the most important filtration operation in the production of beet sugar is that occurring at the so-called first carbonation filters. To these filters comes a slurry equivalent in weight to about 150 per cent on beets, containing about 11 per cent solids in solution, and 3 per cent to 4 per cent solids in suspension, having a total

alkalinity of .10 grams CaO per 100 c.c. and a temperature of 90° C. This juice is the raw juice from the beet, heated, treated with quick lime and carbonated to the point named, in a batch treatment. Slight, almost imperceptible variations in the character of the precipitate may be introduced because of the batch operation.

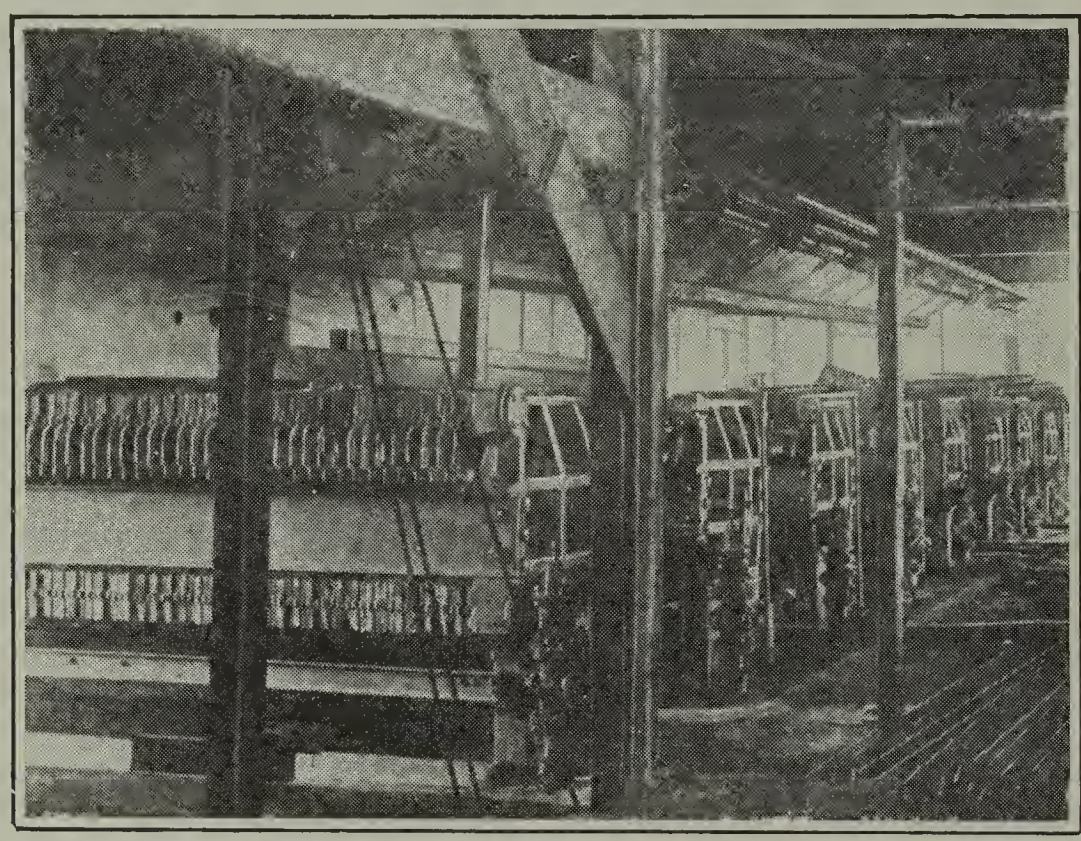


Fig. 1. A Typical Installation of Plate-and-Frame Filter Presses Used in a Large Beet-Sugar Plant for First Carbonation Filtration.

Re-solution of some of the precipitated beet non-sugars is likely to occur if there is delay between carbonation and filtration, and this seriously affects the quality of the crystallized product. For the best results the filtration must be rapid and complete and the filtrate sparkling.

At the time of the wide development of the industry in this country, which occurred about 1900, the common type plate and frame filter was installed for this service. Although various attempts at improving upon the plate and frame equipment have been made, no ultimate apparatus has yet been brought forward. Some of the later developments have advantages, but usually at the expense of some desirable feature. As a result of this lack of development of a filter which shows advantage in each respect the beet sugar operators have been slow to abandon the old plate and frame installations, waiting for a filter which combines at once low

maintenance, low labor cost, low cloth consumption, and low losses. One large company still handles over 60 per cent of its tonnage through plate and frame presses.

Experimentation and trial, however, have not been at a standstill. Among the various newer type filters used for first carbonation purposes may be mentioned the following:

The Kelly Filter, which consists of a horizontal cylindrical steel pressure shell, having one end open, the closed end dished. The

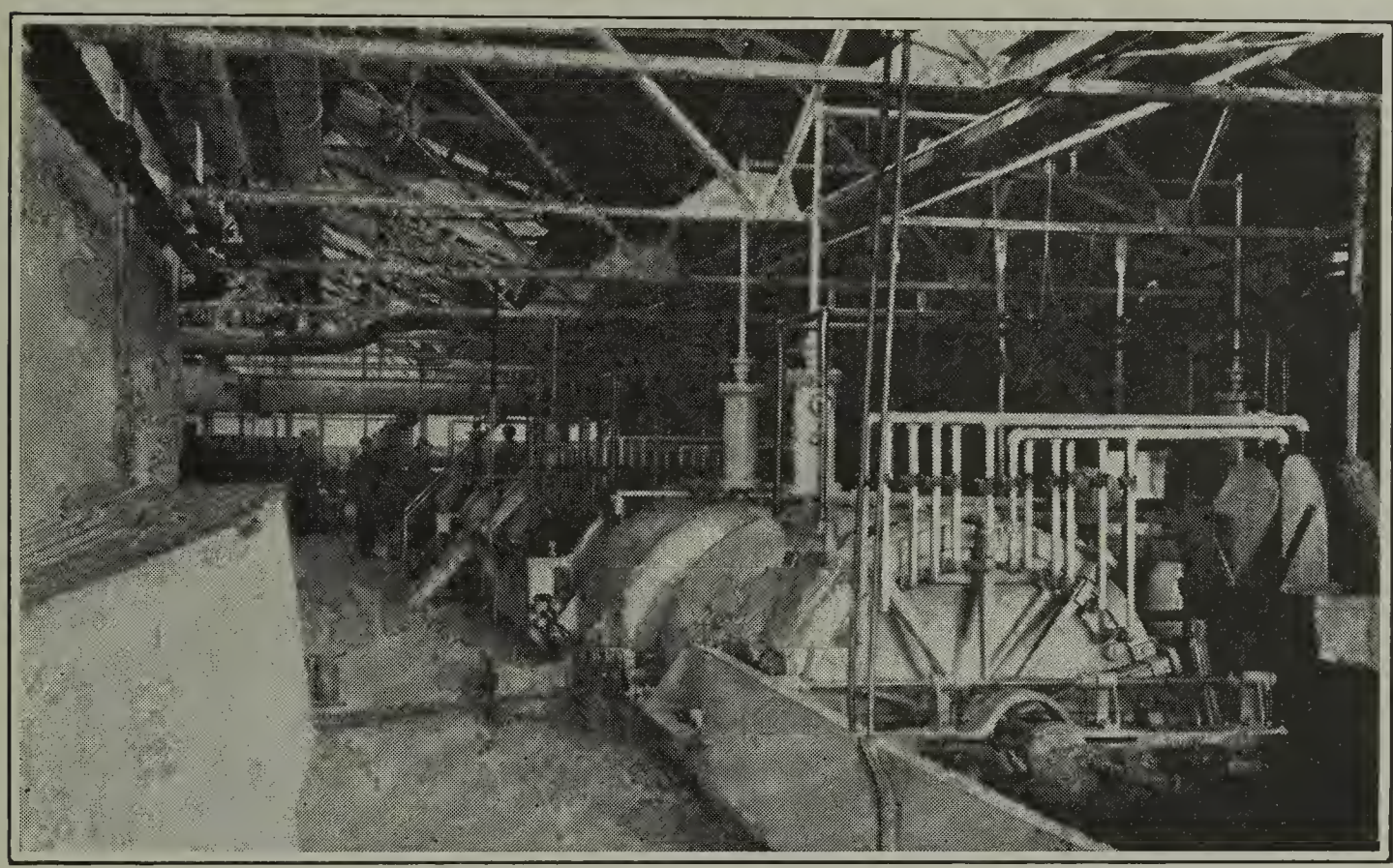


FIG. 2. Kelly Filters Installed for First Carbonation Filtration.

cast iron head which closes the shell is integral with the filter carriage, which holds in position the filter leaves. The inside end of the filter carriage rolls on wheels on a track within the shell and the head end on wheels on a track outside the shell. The carriage passes into the shell and the front head closes the front end of the shell. The leaves are made of iron pipe and heavy woven wire. They are rectangular, of the same length, but of varying widths, and are fastened to the head by pipe unions and nipples. The filtrate passes through these connections, through the head and out of the press. The dressing for the leaves comes in made-up bags which are slipped over the leaf frames and securely sewed. The cycle consists of building cake, washing cake, removing cake, which

is done by unlocking the closing mechanism and rolling the filter carriage out of the shell. The cake is removed by an operator with a hose having a long nozzle delivering a jet of water.

Several indicators to show thickness of cake have been tried, but none have proven very satisfactory. The operator, from experience, judges the thickness of the cake by lapse of time and rate of flow. Occasionally cakes are built so thick that they touch and it is impossible to wash them. On the other hand, it is important to build a sufficiently thick cake in order to get capacity from the installation. Usual thickness varies from 13/16 in. to 1 in.

Between the operations of filling and washing and between washing and removing cake, the shell is drained. In the meantime cakes are held in their vertical positions by air at about five pounds pressure, which is admitted automatically whenever pressure conditions within the shell demand. The handling of these "excess solutions" requires suitable tanks and pumps. During the filling and washing portions of the cycle it is also important to have a sufficient and constant supply of air in order to prevent the cake from falling from the frames during a momentary interruption of supply. This feature is taken care of by a float valve on the top of the press, which prevents escape of liquor and admits air when necessary. It is important that this valve seats properly and works freely and to aid in accomplishing this a small clear water line is installed to flush this mechanism occasionally. Unless this part of the mechanism is in good working order, cakes will leave the cloth and expose an area through which wash water will pour, leaving remaining cakes unwashed.

There is some tendency to build thicker cakes at the bottom of the leaves on account of the subsidence of heavier particles of the precipitate and on account of foam conditions at the top. This tendency is corrected to a large extent by slightly opening the valve on the decanting line which leaves the shell from the top of the cylinder and spills a small quantity of slurry back to the supply tank.

The Kelly filter has considerable advantage over the plate and frame filter in the items of labor and cloth and in the fact that it has only one joint to maintain, but loses this advantage in the item of values left in the cake and in the quantity of wash water required.

Theoretically the Kelly leaf should lend itself to easy washing, when it is considered that the cake when finished should have

equivalent permeability over its surface. Also the flow of wash water through the cake is in the same direction as that which the liquor took when the cake was built, and consequently there is no derangement of the structure of the cake during washing. In actual operation, with the equipment in good working order and with careful handling, no cakes ordinarily drop from the cloth. The one possibility, however, which is always present, is the shrinkage cracks occasioned by the air drying of the cake during the process of draining the shell of excess juice before washing. When this happens, the area surrounding the shrinkage cracks will take a larger proportion of the wash water than is necessary and other areas will not have sufficient water. A possible remedy—though a makeshift—for such a condition and to my knowledge one that has not been tried, would lie in adding to the wash water a certain proportion of spent cake or Kieselguhr to fill up the cracks.

The Vallez Filter.—One trial installation was made of the Vallez filter on first carbonation service. The Vallez filter consists of a cylindrical, horizontal pressure shell having a scroll at the bottom for the delivery of cake through a suitable opening. The shell is split on the horizontal diameter, flanged and bolted. Through the center is a hollow revolving shaft carrying circular leaves of woven wire covered with cloth, regularly spaced on the shaft and ported to allow filtrate to pass from the leaves into the hollow shaft, thence out of the filter.

The filter is intermittent in operation, the cycle being similar to that of the Kelly. The cake is discharged by opening the bottom door, starting the scroll and removing the cake by water jets introduced through doors provided for the purpose, which are situated in a horizontal line in the top half of the shell.

Much difficulty was experienced with broken cloth and in discovering which cloth was broken. The renewal of a broken cloth is an arduous task necessitating the removal of the top half of the shell, removal of shaft and subsequently the discs from one end of the shaft until the disc giving trouble is encountered. These filters were abandoned for first carbonation service, but were equipped with Monel metal cloth and put into the hot saccharate service. This hot saccharate solution is so caustic as to require renewal of a cotton cloth every 24 hours and this consideration makes the Monel-equipped Vallez a fairly good filter for hot saccharate filtration.

The Sweetland Filter is used in a limited way for first carbonation service, but the writer has no intimate experience with its operation. The filter consists of a horizontal cast iron pressure cylinder, split horizontally and the lower half hinged to swing open for the discharge of cake. The leaves are circular and stationary, each having a connection at the top through the shell by a nipple having washers and nut. The nipple serves the double purpose of fastening the leaf to the shell and of providing an outlet for the filtrate to the outlet header outside the filter. Each leaf has a cock on the discharge for shut off in case of cloudy filtrate, which can be observed through glass tubes through which each leaf discharges.

The operation is considerably like that of a Kelly filter and it has the advantage over the Kelly of having less unoccupied volume to produce "excesses." It has advantage over the Vallez in that cloudy leaves are more easily detected and more easily removed and changed. All of the types considered heretofore have the common objection of being intermittent in operation, which necessarily influences cost of installation and cost of operation.

With the present knowledge and experience of filtering first carbonation slurry, I believe it is safe to say that the best thought tends toward the use of a thickener and the handling of the thickened sludge over a rotary vacuum filter. This combination of apparatus seems to answer most fully the requirements of low labor and cloth costs and low losses. Following are the results of some trial installations of this kind:

The Dorr Thickener.—A trial installation of the Dorr thickener followed by a rotary vacuum filter, having a capacity equivalent to about one-fifth of that required for one factory, was installed and operated for a period of 38 days. The Dorr thickener was of the familiar tray type consisting of a tank in which a slowly revolving mechanism sweeps settled solids to a discharge opening by means of suitable plows and rakes. The feed enters continuously at the surface near the center, the clear liquor continuously overflows and a pump regulates the removal of the thickened sludge from the bottom.

The rotary vacuum filter consists of a cylinder rotating on a horizontal axis, with the lower portion of the cylinder submerged in a tank containing the slurry to be filtered. The surface of the cylinder is divided into sections, the dividing partition being parallel to the shaft. The cylinder surface is covered with permanently

installed screen covered with cloth filtering medium. The total surface is covered with one piece of cloth, yet each section is independent in operation from the next. The cloth is held in position with wire winding. Each section is connected with pipes to a rotary valve situated on the shaft at one end of the cylinder, which controls the vacuum for forming the cake and washing it and for withdrawal of the filtrate and wash solution and which in turn controls the air pressure used for removing the cake. A scraper extending across the face of the press and resting on the wire winding, removes the cake after it has been loosened with air. On the face of it, this

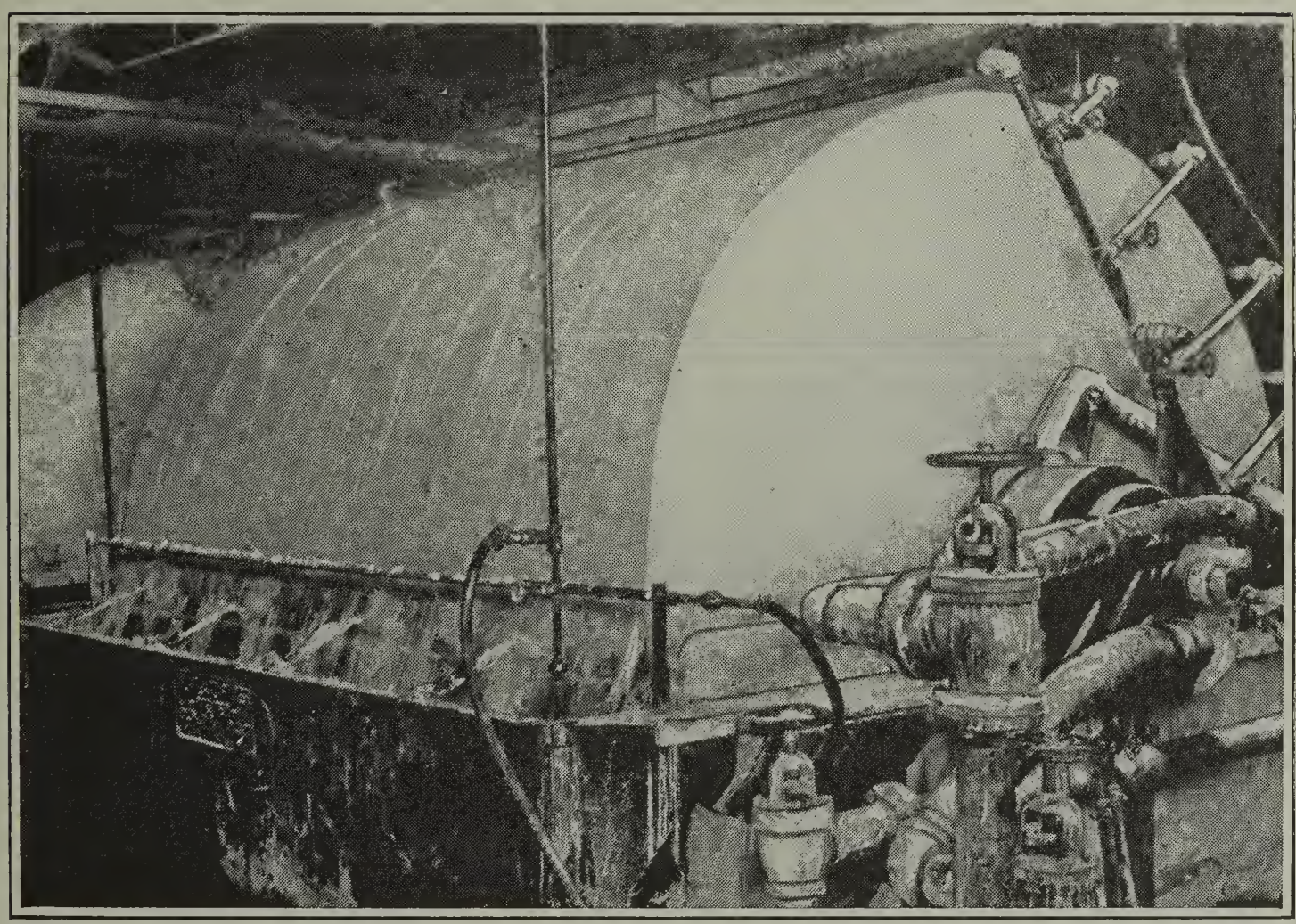


FIG. 3. Portland Filter Following Kelly Filter Used as a Thickener.

combination—Dorr Thickener and Vacuum Filter—presented promising possibilities, but it was found impossible to insure a clear sparkling overflow. It was found that best results were obtained when carbonation was allowed to proceed to a decided break, i.e., to a comparatively low alkalinity. At this point the settling rate was from 3 ft. to 3 ft. 6 in. per hour. Considerable trouble was experienced with gas which collected under the tray and which finally found its way out with the overflow, causing

considerable agitation of the liquor within the apparatus and disturbing the settling conditions, resulting in cloudy juices. It was thought at the time of the experiment that a change of design might correct this difficulty, but this was never accomplished. The cloudy juice seemed not to influence purity appreciably, but the juice was darker and its lime salt content was slightly increased. Since the character of the precipitate which was fed to the Dorr thickener was such that it would not deliver a bright overflow, and this specification is now considered essential, the idea was abandoned.

Kelly Filter as Thickener followed by Rotary Vacuum.—A commercial size of this combination has been in successful operation for four years and shows considerable advantage in all directions. The operation consists in building a cake as ordinarily in the Kelly filter, draining off the excess juice, dropping the unwashed cake, repulping to about 25 per cent suspended solids and dewatering in a battery of rotary filters on which the cake is washed. Filtrate from this operation furnishes water for repulping the Kelly cake. Square feet of filtering area are rather high per unit output with this arrangement, but costs of the essentials—labor, cloth and losses—show advantageously.

The Oliver-Borden Thickener.—Last year an installation of this type was made and operated for 30 days. In size it was equivalent to about one-seventh of the requirement for one factory.

This thickener consists of a steel tank, open at the top, having a rectangular cross section and "V"-shaped bottom equipped with a scroll mixer-conveyor. Suspended in this tank vertically are stationary tapered steel tubes $9\frac{1}{2}$ in. dia. at the top and $8\frac{1}{4}$ in. dia. at the bottom, 6 ft. 8 in. long. The tubes are perforated with $\frac{1}{4}$ in. holes, $\frac{3}{8}$ in. centers and inside of each tube is another tube 6 in. dia. x 12 in. long with solid surface. The perforated tubes are covered with cloth stockings, wrapped with wire and have 16 sq. ft. filter surface. The tubes are arranged in groups of four each. Each group is served with a 2 in. pipe, branching to four $1\frac{1}{2}$ in. pipes, one to each tube of the group, the other end of the 2 in. pipe being connected to the regular Oliver filter valve mechanism that automatically and periodically produces inside of the tubes, vacuum, atmospheric or pressure conditions.

In operation, the tank is filled with slurry submerging the tubes, vacuum produces a cake and clear juice. Momentary breaking of

the vacuum and application of pressure blows off the collected cake, which gathers in the "V"-shaped bottom of the apparatus from which the thickened sludge is removed by a diaphragm pump for further separation and washing on a vacuum drum.

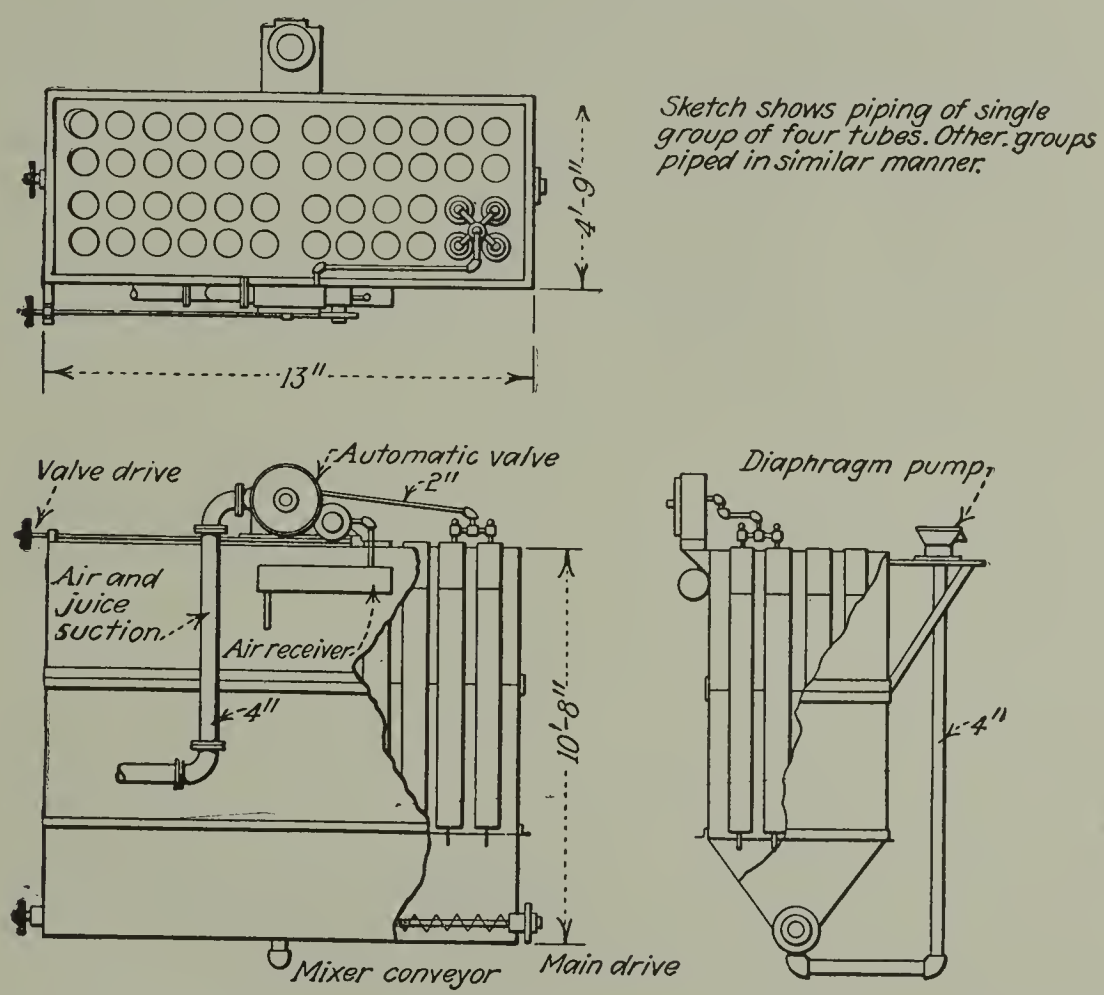


FIG. 4. Sketch Showing Principal Features of Oliver-Borden Thickener.

The cycle, as operated in this experiment, was 10.5 minutes and obviously the last portion of the suction period must have been through an appreciable thickness of cake and the flow through the accumulating cake must have been at a gradually decreasing rate as the end of the suction period was approached. If the above observations are correct, and if the outlet conduits are sufficiently large to carry the filtrate when the cake is very thin, then they are larger than necessary near the end of the suction cycle, consequently the average rate of flow through the cloth must be less than the capacity of the outlet pipes. The capacity per unit filter area might be increased by more frequently alternating suction and blowback.

Thickened sludge showed about 13 per cent solids, the filtrate was clear, labor and cloth low and indications point to low losses. Capacity indications show .98 tons beets per 24 hours per sq. ft. filter area.

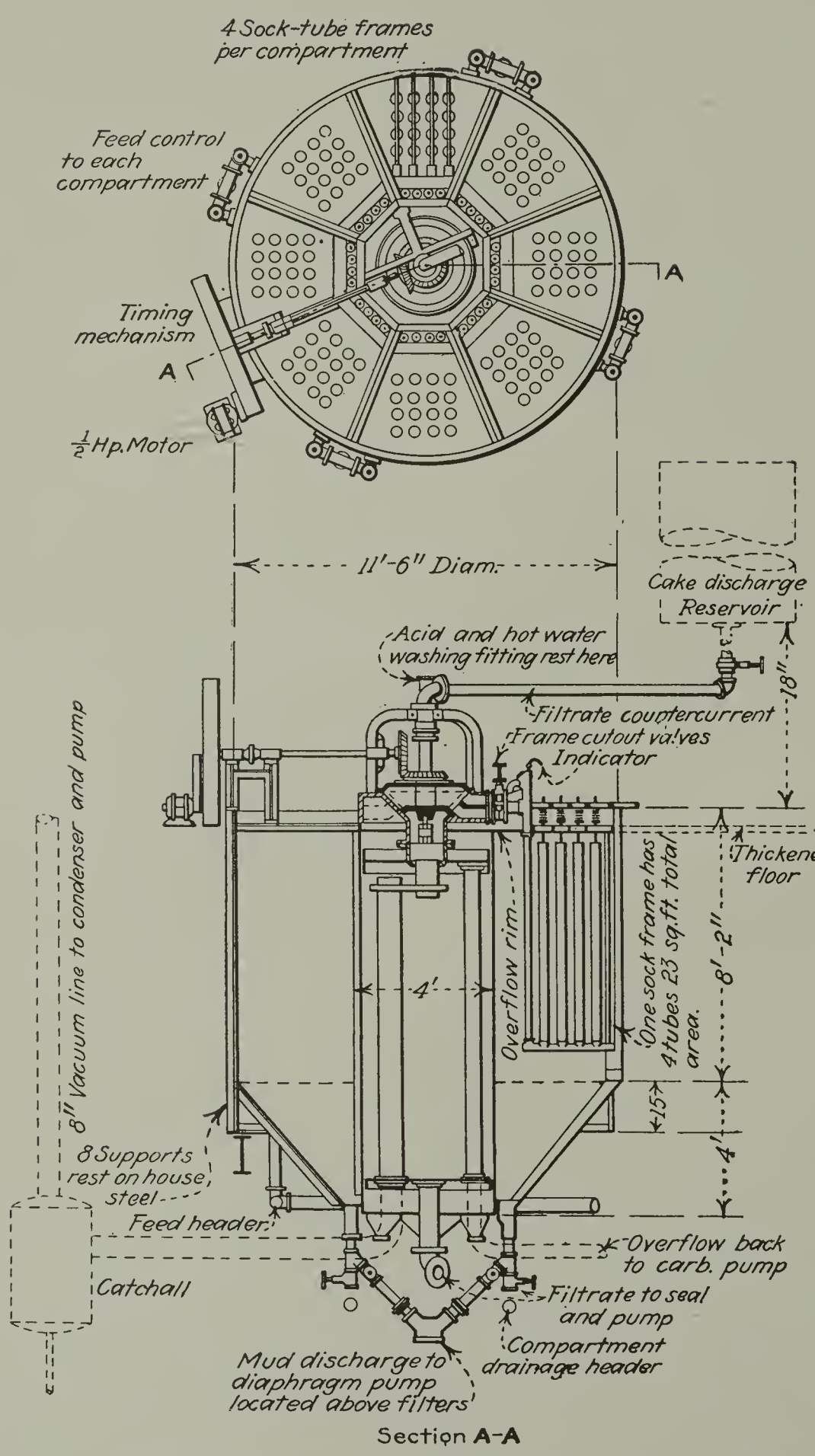


FIG. 5. Sketch Showing Principal Features of Genter Thickener.

The Genter Thickener, in the process of development, operates on the same principle as the Oliver-Borden described just above, except that it uses a hydrostatic blowback instead of air. The thickener consists of two tanks, one within the other. The smaller central tank has closed ends and forms the vacuum receiver. The annular space between the central tank and the outside tank forms the thickening chamber, which is divided into eight sector shaped smaller compartments or units by means of walls that radiate from the receiver. Tubes having 5.75 sq. ft. area are in groups of four, each group connected to a central rotating valve, which periodically allows a vacuum condition within the tube to be alternated with a liquor blowback. The timing arrangement is easily adjusted and I am advised that the results here referred to were obtained with a suction period as short as 30 seconds. The tubes are of wood, covered with cloth sacks not wound, have an outlet connection at the bottom and are held in the tube frame under the tension of a coil spring.

Large claims for capacity are made for the Genter vacuum thickener. The machine is said to have shown capacities equivalent to two to three tons beets per square foot filter area per twenty-four hours. The large capacities are said to be due to the fact that the filtrate travel and hydrostatic blowback travel from the timing valve are short and equidistant and therefore instantaneous in all groups of frames, and also that the vacuum is always immediately active and effective when filtration starts. It is also claimed that this large capacity is due to the frequent hydrostatic blowback, which minimizes the formation of vapor space within the tubes and conduits at the working temperature. Under these conditions it is claimed that the conduits are carrying practically solid columns of liquor rather than successive pistons only of liquor.

For comparative purposes I have set down data regarding some of the apparatus discussed:

I have omitted giving any data on quantity of wash water required to wash the cake produced by these various filters on account of the unreliable figures usually given by a hot water meter in constant use. The water necessary to reduce the losses to the figures shown ranges from 120 per cent to 160 per cent and up on wet cake. These residual values in first carbonation cakes may appear high, especially to metallurgical men, but it must be remembered that any further reduction necessitates more dilution

COMPARISON OF VARIOUS TYPES FILTERS ACTUALLY INSTALLED FOR FIRST CARBONATION FILTRATION SERVICE

	Factory					
	W	W	N	T	V	L
Equipment and rated beet capacity	Plate and frame non-Steffen 2.07 CaO on beets 1436 tons Beets 24 hours	Proposed Oliver-Borden Thickener and Rotary Vacuum*	Kelly non-Steffen 2.17 CaO on beets 1640 tons Beets 24 hours	Kelly Thickener Rotary Vacuum non-Steffen 2.18 CaO on beets 1633 tons Beets 24 hours	Kelly Steffen 3.24 CaO on beets 2604 tons Beets 24 hours	Plate and frame Steffen 3.36 CaO on beets 2720 tons Beets 24 hours
Draft	142	142	161	147	146	146
Tons juice passing 1st presses 24 hours	2,039	2,039	2,640	2,400	4,227	4,466
Tons wet cake at 1st presses 24 hours	145	145	182	185	402	421
Sq. ft. filter surface	3,556	3,246	4,900	4,500	6,623	11,844
Tons wet cake per 24 hours per sq. ft. filter surface	.0408	.0447	.0372	.0411	.0607	.0355
Tons juice per 24 hours per sq. ft. filter area	.573	.628	.539	.533	.638	.377
Operating labor cost per ton wet cake	$.55	.17	.22	.22	.18	.34
Cloth cost per ton wet cake	$.28	.04	.07	.06	.07	.26
Pounds sugar per ton west cake	15	9	20	9	22	18

* Estimated.

and there comes a point where the sugar loss must be compared with the cost of coal and equipment for recovery of the sugar by evaporation.

Saccharate Filtration

Let us pass now to another large filtration problem of the beet sugar industry, that of cold saccharate filtration in the process devised by Steffen for the recovery of sugar from molasses. In this process advantage is taken of the fact that sugar forms an insoluble tri-calcium sucrate when treated with lime. The operation is carried out in an apparatus called a "cooler," consisting of a vertical cylindrical tank having vertical flues through which the solution is circulated by means of a propeller. On the outside of the flues cooling water is circulated. The molasses is diluted to a 5.5 per cent to 6 per cent solution and to this there is added 100 per cent to 120 per cent finely ground lime per 100 sugar, while the mixture is being circulated in the above mentioned "cooler."

After this operation the filtration problem consists in separating and washing the insoluble sucrate from the remaining liquid which is waste. The slurry contains about 12 per cent solids and has a tendency to foam on account of included air introduced during its previous violent agitation. The concentration of suspended solids is high enough for direct handling by vacuum filters without thickening. The sucrate is slightly soluble and is comparatively unstable, making it desirable to quickly effect the separation. There are about eleven tons of slurry per ton of molasses worked. The resulting cake contains 60 per cent water and amounts to 300 per cent on original molasses. Wash water varies from 90 per cent to 225 per cent on cake.

As in the case of the first carbonation filtration, as much as 60 per cent of the molasses worked in the Steffen process is handled with the old plate and frame presses. These presses are large, taking a 40 in. cloth, having a 2 in. cake frame and 1,100 sq. ft. per press. The labor is arduous and at times it is difficult to interest workmen for this kind of labor. The waste solution and the recovered cake are sufficiently caustic with lime as to require workmen to exercise considerable care to prevent severe burns. Notwithstanding these disadvantages of the plate and frame filters, they have endured against newer installations of rotary vacuum filters, etc., and this largely on account of the lesser loss shown by

the plate and frame equipment. On the average, losses are greater on the vacuum filters than on plate and frame to an extent equivalent to 2 per cent of the total sugar entering the process.

There are several reasons for this difference. The vacuum filter picks up a $\frac{3}{4}$ in. cake, which is washed with 100 per cent water on cake. To date we have not been able to definitely separate the resulting wash solutions from the original filtrate in a satisfactory manner. Just why this condition exists is not known. Suspicion points to the probability that air locking occurs in the filtrate discharge passages, which prevents them from draining completely and thus causes a mixing of filtrate with wash solutions in these

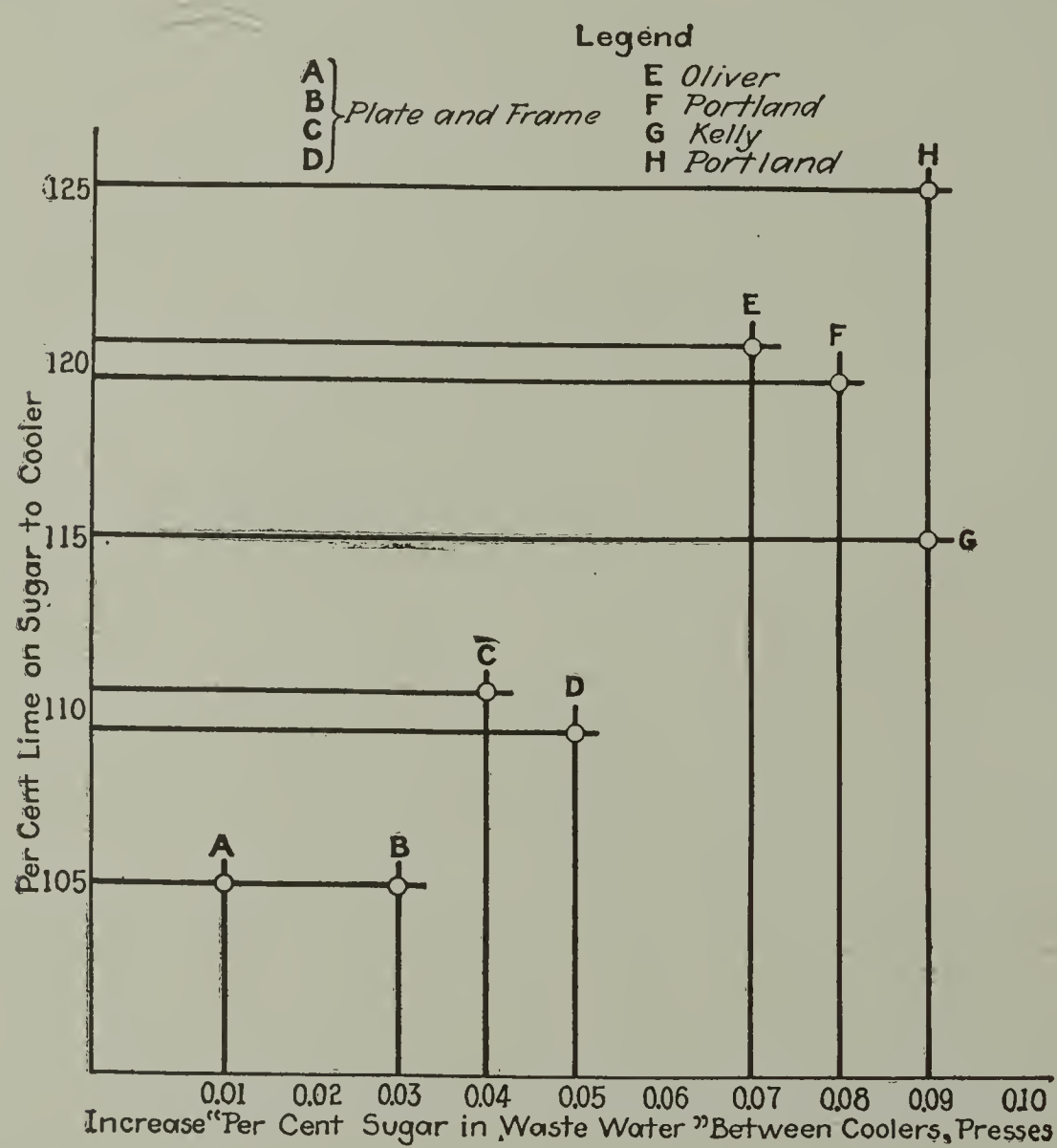


FIG. 6. Comparing Different Types of Filter on Cold Saccharate Under Varying Operating Conditions.

spaces. On the other hand the plate and frame press with a 2 in. cake washes with 125 per cent to 250 per cent water on cake, but the separation of the wash water from the waste water is fairly

complete. Wash solution contains a small percentage of sugar and as the quantity of the wash water is increased the proportion of sugar to non-sugar is increased. If separated from the waste water the wash solution has a valuable use for the dilution of the original molasses, which not only conserves on quantity of water used and quantity of water discarded as waste, but coincidentally saves sugar.

Another fruitful source of loss in operating a vacuum filter on cold saccharate is the necessity for maintaining an overflow from the filter immersion tank to free the contained slurry of foam. Although this overflow contains fewer suspended solids than the feed, the longer time of contact between solids and solution tends to cause re-solution of the precipitated saccharate, thus increasing losses. In the installations which show an excessive re-solution there usually appears a slightly higher lime addition. Work is now being done to determine whether this condition is a function of the type of press, of the lime, or of some other detail of operation. The point may be more clearly brought out by consideration of the following graph:

The American Filter has been tried on cold saccharate with only limited success. The principle of the American is on the order of the Oliver and Portland, except that instead of having a cylindrical drum divided into compartments to carry the filtering medium there are a number of vertical discs on a rotating shaft which carry the cloth. This apparatus on cold saccharate service developed excessive foam troubles; it was difficult to keep the cloth cleaned on account of inaccessibility and the fact that the scrapers used to remove the washed cake plastered the precipitate into the pores of the cloth. It was found difficult to wash a vertical cake with sprays. In general the filter required too much attention to attain much success in sugar work. I am advised that large presses of this type are successfully used on ore slimes.

In conclusion, present indications point to the more extended use of the rotary vacuum drum type filter for cold saccharate work, especially if some remedy can be found to correct high-loss and high-lime-addition characteristics now existing, and as noted before the trend of thought for betterment of the first carbonation filtration lies in the direction of a suitable thickener followed by a continuous vacuum filter.

Discussion

President Reese: This very splendid paper is open for discussion.

Mr. William C. Bainbridge: I should like to ask how the life of the Kelly press compares with that of the plate and frame?

Mr. Maudru: It is very much better. One can get a better idea of that by cost conditions (referring to lantern slide). Here is the Kelly non-Steffens, that costs seven cents a ton, per ton of wet cake; here is a plate and frame non-Steffens, twenty-eight cents, and the one over there is a plate and frame Steffens, at twenty-six cents. I think that will give you an idea of the cloth life.

Mr. Richard B. Moore: Mr. President, the statement made by Mr. Maudru about colloidal material being in the overflow of the Dorr thickener is quite true. I would not want anyone present to think that the Dorr Company had given up this problem because it could not be worked out in a relatively few days in connection with regular commercial operation. As you all well know, experimental work on a large scale frequently seriously interferes with plant operation and conditions cannot always be varied to the extent that is desired. We are now doing what perhaps we should have done at the very start, namely, doing the experimental work in question on a semi-commercial scale so that the various factors involved can be much better controlled.

The Great Western Sugar Company has given us excellent cooperation in connection with the semi-commercial installation which the Dorr Company put in at the Brighton Plant last season, and which we hope to continue to use this campaign.

We are not only interested in producing a satisfactory precipitant in connection with first carbonation, but also to try and develop a continuous automatically controlled carbonation which would, if successful, give many advantages.

President Reese: Are there any further remarks?

Mr. Phillip H. Groggins: May I ask whether the Haubold filter has ever been investigated for its filtration?

Mr. Maudru: Not to my knowledge. It may have been.

Mr. Groggins: It is automatic entirely. I know it has been used in Germany. It is not used for all kinds of carbonation.

Mr. Maudru: Is it a pressure filter?

Mr. Groggins: It is a pressure filter, vertical type, operating

like a large fly-wheel. It is centrifugal, it is continuous and automatic.

MR. MAUDRU: I don't know anything about it.

MR. CROSBY FIELD: I might say in answer to Mr. Groggins' question, there are about four of those filters, for continuous centrifugal, I think are called, in this country. Lungivitz, of Jersey City, will give you the information.

THE HOT SACCHARATE PROCESS OF THE BEET SUGAR INDUSTRY

A Discussion of the Chemical Engineering Involved in the Recovery of the Final 10 to 15 Per cent of Sugar by the Hot Saccharate Process as Operated Commercially in Four Plants

By R. W. SHAFOR,

Read and discussed at the Denver Meeting, July 16, 1924

The Hot Saccharate Process, as used in America, is not one of the most important steps in the beet sugar process from an economic viewpoint but it is often one of the most troublesome from the standpoint of the factory operator. This is probably due to the fact that, so far as general usage is concerned, it is still in its infancy. The first installations were, I am informed, two or three

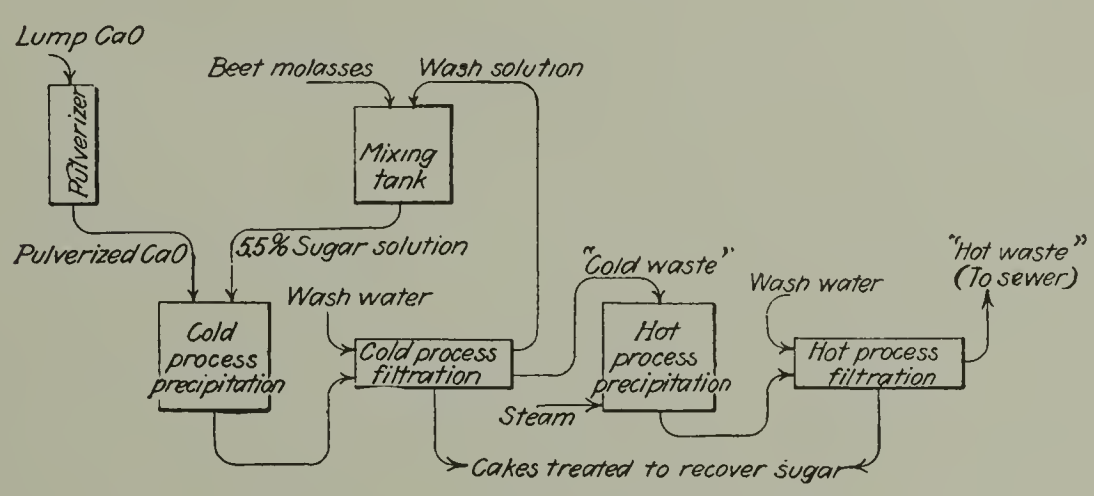


Fig. 1. Flow-sheet for the Steffens process.

in number and were made about twenty-five or thirty years ago. Aside from these, no installations were made until about 1915 when, with the advent of war-time sugar prices, it became more attractive economically. During subsequent years it has come into rather general use throughout the industry in this country and with this has come a considerable development which appears to insure it a permanent place in the Steffens process flowsheet.

The accompanying diagrammatic flowsheet, Fig. 1, illustrates the Steffens Process for the recovery of sugar from beet molasses. It may be divided into two sub-processes, the first known as the Cold Saccharate Process and the latter as the Hot Saccharate Process with which this paper is concerned. A brief description of the operation of the two will probably assist those not familiar with beet sugar operations toward a better understanding of that which is to follow.

In the Cold Saccharate Process, beet molasses is diluted so as to form a solution containing approximately 5.5 per cent sucrose and this solution is treated, usually at a temperature of 15° C., or less, with finely powdered lime in sufficient quantity to precipitate from 85 per cent to 90 per cent of the sugar present. The resulting precipitate is separated from the "mother" solution by filtration and subsequent washing. The solutions resulting from washing the filter cakes are usually employed in diluting molasses to be treated. The "mother liquor," known as "Cold Waste," in addition to most of the impurities which were present in the original molasses, contains sugar to the extent of from 0.5 per cent to 0.8 per cent and a quantity of lime. This "cold waste" is the raw material from which sugar is recovered by the second or hot saccharate process.

The hot saccharate process consists of two operations. The first of these involves heating the "cold waste," above mentioned, to a temperature of approximately 80 deg. C., which procedure causes the formation of a precipitate consisting of sugar and lime. Lacking a more definite name, this precipitate is generally termed the "Hot Saccharate Precipitate." The second operation consists merely of separating this precipitate from its mother solution, known as "hot waste," which is discarded.

The basic chemistry involved in the Steffens process deals with the compounds of calcium oxide and sugar. These compounds are generally considered to be addition products with the general formula $X\ CaO.C_{12}H_{22}O_{11}$ and are relatively unstable. A number of such compounds are described in the literature but those with which we are most concerned contain four or less molecules of CaO per molecule of sugar. In the cold saccharate process the precipitate formed is generally believed to be the tricalcium saccharate, $3CaO.C_{12}H_{22}O_{11}$. The precipitate formed in the hot process, as we shall show later, is probably the tetra-calcium saccharate, $4CaO.C_{12}H_{22}O_{11}$.

Little information, of value or otherwise, has been published and probably not a great amount is known of the detailed chemistry of the hot process. The data presented here on this phase of the subject are the result of investigations made by the research organization with which the writer is associated and while not complete are considered dependable.

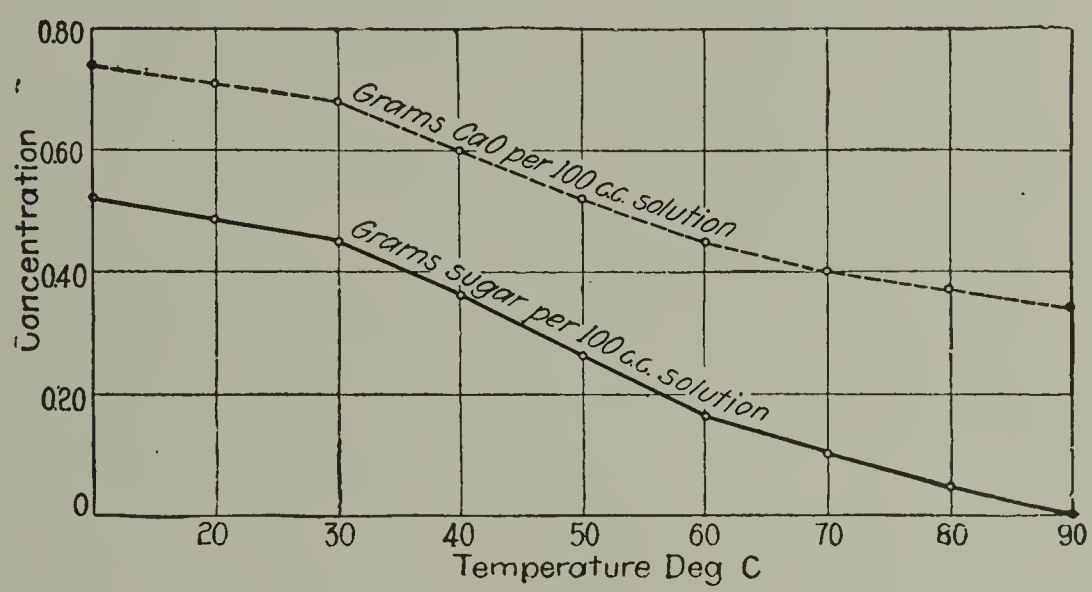


FIG. 2. Precipitation-Temperature Curve for Hot Saccharate.

The curves in Fig. 2 illustrate the typical precipitation-temperature curve involved. In this particular case the "cold waste" solution contained 0.52 per cent sugar and an alkalinity equivalent to 0.74 per cent CaO at 10° C. A quantity of this cold solution was heated to 30° C. and the precipitate filtered out to produce a solution with sugar content and alkalinity as plotted on the 30° abscissa. Another quantity was heated to 40° C., and so on until at some point between 80 and 90° C. the resulting solution showed a neutral polarization.

At first glance these curves would seem to justify the conclusion that the precipitation involves simply the temperature-solubility relationship of a compound which is present in the "cold waste." Data, to be given, indicate, however, that such is not the whole case and that a chemical reaction equilibrium is probably involved.

On this point the curves in Fig. 3 indicate that a hot waste free from sugar is not always a possibility. These curves represent the temperature-sugar concentration relation obtained as in Fig. 2, when cold wastes containing 0.48 per cent, 0.72 per cent and 0.87 per cent sugar are heated to the temperatures indicated and the precipitate removed. It will be noted that the lower curve which re-

sulted from heating the 0.48 per cent sugar cold waste yielded a final waste containing no sugar; that the treatment of the 0.72 per cent cold waste resulted in a final waste containing 0.10 per cent sugar and that the 0.87 per cent waste gave a final figure of approximately 0.22 per cent sugar. From these curves two deductions are apparent.

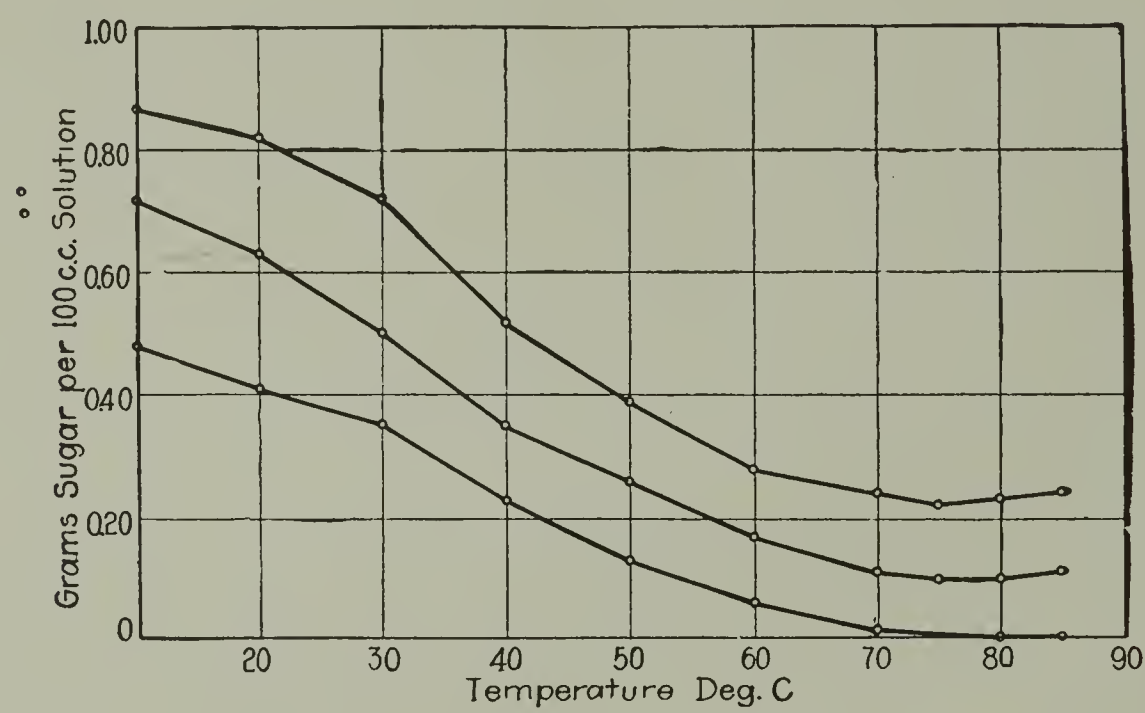


Fig. 3. Relation between Temperature and Sugar Concentration in Heated Wastes.

First—That for all concentrations of sugar in the cold waste (within the range covered) a temperature of from 75° to 85° C. yields the maximum recovery.

Second—The quantity of sugar remaining in the final waste is a function of the concentration present in the cold waste treated.

The logical conclusion with respect to the latter of the above deductions is, of course, that there is present insufficient lime to precipitate all of the sugar from the "cold wastes" containing the higher concentrations of sugar. This conclusion appears to be justified from the data plotted in Fig. 4.

The upper curve in this figure represents the relative precipitation of the sugar—per cent on total sugar in the cold waste—corresponding to the "cold wastes" treated as indicated on the abscissa. This curve indicates the same relation as was shown by the curves in Fig. 3 in that the percentage precipitation falls off as the sugar concentration in the cold waste increases.

In obtaining the curve representing the CaO available in cold waste for sugar precipitation the alkalinity of the hot waste resulting from the experiment was substracted from the alkalinity of the cold waste treated, both figures being expressed as CaO. This is justified on the basis that, the alkalinity of the hot waste is a constant for a given molasses and for a given method of cold process operation regardless of the concentration of either sugar or alkalinity in the cold waste, or the sugar content of the resulting hot

FIG. 4. Relation of "Available CaO" in "Cold Waste" to Sugar Precipitated.

waste. Thus the alkalinity of the cold waste is composed of a constant quantity of alkali, probably a mixture of potassium, sodium and calcium which is not available for sugar precipitation and a variable quantity of lime which is available for sugar precipitation. The correlation between this curve and that for the per cent sugar precipitated is obvious.

A further analysis of these data indicates that this variable quantity of available lime may be a function of two factors present in the "cold waste" solution. In Table I, the figures in Column I represent the per cent of sugar in various "cold waste" solutions produced from a given molasses. In column II is given the available CaO—per cent on solution—present in each of the solutions.

Now, there are available, data which indicate that the sugar in any "cold waste" is combined with lime to form a soluble compound having a probable composition $3CaO.2C_{12}H_{22}O_{11}$. Calculations, on this basis, indicate that the quantity of lime combined with sugar in the various cold wastes tabulated, is as listed in column III. Thus in the waste which contained 0.47 per cent sugar, 0.12 per cent CaO, of the total available (0.37 per cent) CaO in solution, was probably combined with sugar. By difference, in column IV, this leaves 0.25 per cent CaO (on solution) to be supplied from some other source within the solution. Now it is interesting to note that the lime from this second source within the cold waste is apparently a constant and independent of the sugar concentration. Thus, it would appear to be a possible function of some impurity present which very obligingly carries lime in a chemically combined form from the cold process into the hot where it releases it for sugar precipitation. Again it may be partly due to the lower solubility of lime in aqueous solution at higher temperatures.

Thus, there are probably two chemical reactions involved. If the sugar in the cold waste is combined as sesqui-saccharate and the alkalinity of the hot waste is independent of sugar concentration any

TABLE I.

Sugar in Cold Waste (Per Cent on Solution)	Available CaO in Cold Waste—Per Cent on Solution		
	Total	Combined as Sesqui-Sacch. (Calc.)	Difference Total—Combined with Sugar
0.47	0.37	0.12	0.25
0.52	0.39	0.13	0.26
0.62	0.42	0.16	0.26
0.78	0.46	0.20	0.26
0.88	0.48	0.22	0.26
0.94	0.49	0.24	0.25
1.04	0.51	0.26	0.25

sugar in the hot waste is probably not combined with lime. Thus it would appear that with cold wastes, in which the sugar concentration is high, some sesqui-saccharate must react with other to produce the precipitating compound and free sugar. The second reaction probably occurs between the CaO-impurity compounds, above postulated, and the sesqui-saccharate.

This brings us to a consideration of the molecular composition of the precipitate and the data plotted in Figue V may throw some light on this point. This curve represents the ratio of the mols lime per mol of sugar present in precipitates resulting from treating cold wastes in which the sugar concentration varied from 0.44 per cent to 1.10 per cent. In the range from 0.5 per cent to 1.0 per cent sugar (in cold waste treated) these data indicate a probable precipitate composition of $4CaO.C_{12}H_{22}O_{11}$. This conclusion cannot,

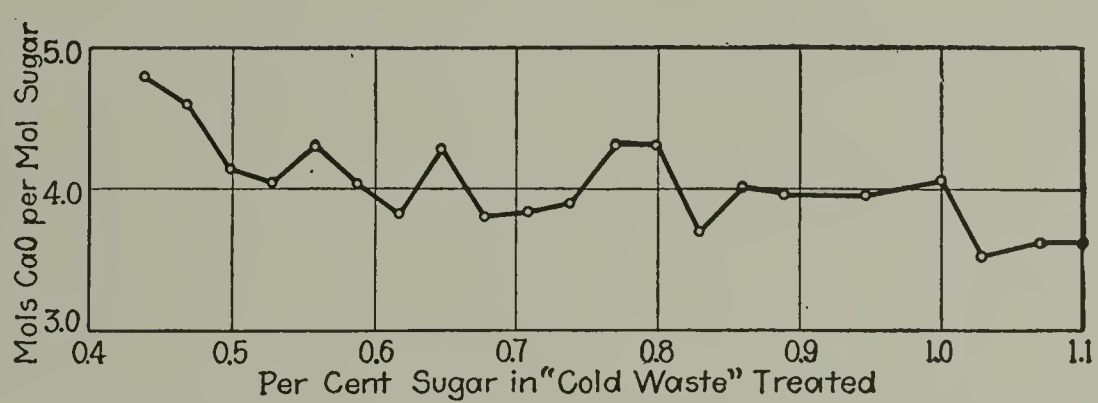


FIG. 5. Ratio of Mols CaO to Mol Sugar in Hot Saccharate Precipitate obtained from Various Cold Wastes.

of course be definite with such variations as shown, but when the experimental error introduced by the polariscope operated on dilute solutions containing a relatively high concentration of impurities is taken into consideration, the correlation appears more probable. It will be noticed that, in the ranges above 1.0 per cent sugar in the waste treated, the ratio is apparently something less than 4:1. As such concentrations are seldom encountered in practical operation, this result has not been subjected to extensive study. At the other end of the curve, with concentrations of less than 0.5 per cent the ratio is greater than 4:1, a fact which indicates that that lime which is present in the cold waste as available for precipitation, is precipitated during the heating whether or not there is sugar present with which it may combine.

As a further indication along this line we have factory operation results over a period of years which show occasionally a molecular ratio of less than 4CaO to 1 sugar in individual tests. The lowest average ratio, resulting from an operation of from 75 to 100 days which has come to our notice, is approximately 4.5 CaO to 1 sugar.

And this brings us to our last point in connection with the chemistry of the process. If a cold waste be heated to the proper tem-

perature for obtaining a maximum precipitation of the sugar present, say 80 deg. C., and subsequently cooled to some lower temperature, say 60 deg. C., where the precipitate is filtered off, a dissolution of sugar takes place so that something less than the maximum possible precipitation of sugar is obtained and the ratio of CaO to sugar in the precipitate is increased. Further, only a portion of this redissolved sugar may be recovered on reheating the mixture to 80 deg. C. before filtration. This indicates the necessity for rigid temperature control throughout the heating and filtering operation, and is the probable cause for the excessive ratio of mols CaO to mol sugar in factory precipitates.

The commercial existence of the Hot Saccharate Process depends upon its ability to recover the last 10 per cent to 15 per cent of the sugar introduced into the Steffens Process more economically than is possible with the cold process alone. The principle items of cost in its operation have been

First—Filter fabric for the separation step.
Second—Steam for the precipitation step.
Third—Labor.

The life of cotton filter fabric in this service is limited to approximately 24 hours operation. Deterioration, resulting from the action of the hot alkaline solution, causes a marked decrease in the tensile strength together with a hardening of the cloth. As a result the consumption of cloth, when plate and frame filters are used, is often as much as 30 to 35 square feet per ton of molasses worked. This excessive cost has been the cause for considerable effort towards supplanting this type of filter.

One attempt in this direction has been based on employing the Vallez pressure filter which permits the use of metallic filtering mediums. The character of the precipitate, however, had been such as to render necessary the employment of some filter aid such as Kieselguhr. This is usually applied as a coating to the metallic cloth before the precipitate is introduced into the filter.

Another line of attack is based on the use of the Dorr tray thickener and the rotary vacuum filter. With this equipment something between 50 per cent and 75 per cent of the waste is separated from the precipitate by decantation and the remainder sent to the filter in the thickened sludge. It is necessary to insulate the thickener tank to avoid heat losses and to steam jacket the tank of the filter

for a like purpose. Cotton fabric is employed as filtering medium and, while its life is still limited to approximately 24 hours, the cloth consumption is approximately 1.5 square feet per ton of molasses worked or 5 per cent of that required for the plate and frame filters. Of these three installations the last, of course, requires the least operating labor.

In connection with hot saccharate filtration it would seem that continuous operation, such as is provided by the latter equipment, is preferable to the intermittent procedure necessary with the two previous types on the basis of improved temperature control. As mentioned previously, the precipitate decomposes if it is allowed to cool and the thickener-vacuum filter combination appears more foolproof against temperature fluctuations.

It is subject, however, to two difficulties. Variations in the physical character of the precipitate affect both units to a greater extent than in the case of the pressure filters. Also, a considerable quantity of foam is sometimes discharged from the precipitation tanks and this accumulates on the surface of the thickener unless provision is made for its removal. This latter is probably more of an eyesore than an economic disadvantage. It seems to follow the incorporation of air into the cold waste enroute to the hot saccharate process and, where means for permitting the escape of this gas are available, gives little trouble.

The variable physical characteristics of the precipitate, however, was economically menacing, since it caused a definite loss of precipitate with the decanted solution from the thickener. This has been solved by incorporating an idea, new to the process, into a new precipitation unit. With this unit it has been possible to produce not only a more uniform product but, also, a product which settled more rapidly and filtered more easily than the previously obtained precipitates.

Von Veimarn's "law of corresponding states for the crystallization process" states that the relative degree of dispersion of any precipitate formed by condensation methods may be expressed by the equation

$$d = \frac{C}{S} \cdot n.$$

In this expression, "S" represents the solubility of the substance

being precipitated measured in the usual manner, say mols per liter. "*C*" represents the quantity of the substance present as "potential" precipitate or in other words the quantity present as "supersaturation." "*n*" is the viscosity of the solution. "*d*" is the degree of dispersion which is larger for more finely divided precipitates. Thus, it would appear that, if a physically uniform hot saccharate precipitate were to be obtained, the quantity C/S should be controlled. Further, if a satisfactory method of reducing this ratio could be had a coarser precipitate would result.

W. D. Bancroft of Cornell University has commented on this equation to point out that it contains no factor for the effect of agitation during the condensation process. He further indicates that increased agitation usually operates to increase the degree of dispersion.

There is no record in the literature of any effort to apply these conceptions to the precipitation of hot saccharate.

Reasoning deductively on the basis that the quantity of tetracalcium saccharate precipitable, if such is the composition of the precipitate, is a function of the lime available in the cold waste and, further, that where sufficient lime is present the polarization of the hot waste may be reduced to zero, it would seem that the solubility "*S*" of the compound would be very low especially at the "finishing temperature," 80°-85° C. Such a solubility would tend to give an excessive ratio for the C/S factor and would indicate that variations from this source might easily be the cause for the filtration difficulties encountered.

The controlable quantity in this ratio is obviously the quantity of "potential" precipitate, "C," which is present at any instant during the precipitation process. To control and decrease this quantity two possible methods of continuous operation are apparent. The first of these consists in effecting the precipitation in a series of steps in which the supersaturation present at any time would be regulated by temperature control. With this method great care would be necessary to avoid localized over heating at the points of steam introduction. Further, a number of steps would be required with a corresponding multiplication of temperature controlling equipment if any appreciable decrease in the C/S ratio were to be obtained. The second possibility consists of diluting the cold waste so that the desired result can be obtained in a single step. Obviously,

the diluting substance employed must be chosen so as to avoid any reduction in the amount of sugar recoverable by the process. The latter has been chosen as the more economical and fool-proof of the two.

As commercially applied, during the 1923-24 campaign, the process consists of diluting one volume of cold waste with approximately 40 volumes of hot waste which is practically free from precipitatable substance but which has not been separated from the

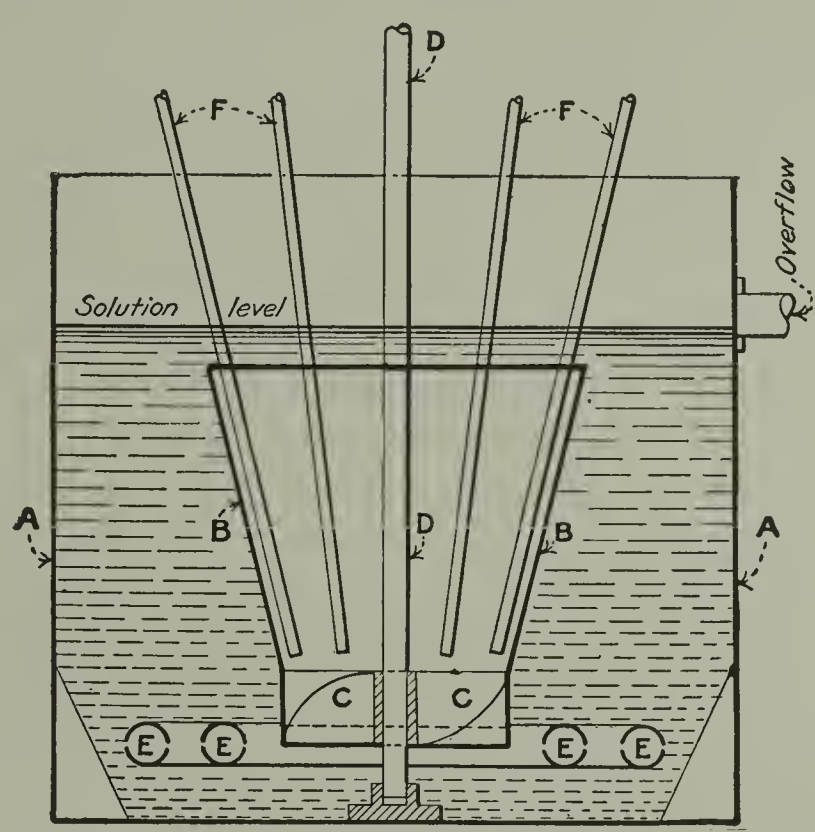


Fig. 6. Sketch of Hot Saccharate Precipitation Tank.

saccharate precipitated from it. The introduction of the comparatively small amount of the cold solution into the large volume of the hot is, of course, accompanied by a relatively rapid rise in the temperature of the former. Unless diffusion or mixing of the two is assisted by mechanical means this feature may defeat the object of the process. Thus, it becomes advisable to effect the mixture in a zone of mechanical agitation and when this is done the desired results may be obtained. The presence of the precipitate in the diluting solution assists in keeping down the number of new precipitate nuclei formed, once the mixture has been effected.

As to the apparatus employed,[1] Fig. 6 illustrates that operated in

[1] Author's Note: Apparatus described herewith is protected by United States Patent.

four factories last year. It consists of a cylindrical tank (*A*), in which is installed a central well (*B*). A four-bladed propeller of the ship type (*C*) is mounted on a vertical shaft (*D*) in the position shown inside and at the bottom of the well. Both the well and the annular space between the well and tank walls are baffled so as to prevent swirling. Thus a definite path of travel is provided for the tank contents with a downward direction inside the well and upward thru the annular space. Perforated steam coils (*E*) were installed near the bottom of the annular space so that heating might be effected in this zone.

Thus, there is created a stream of tank contents down the central well carrying a fairly definite volume per minute which may be used as a dilutant, if sufficient time for precipitation is provided in the annular space. Under these conditions approximately 30 seconds is sufficient for this purpose. This requires that the tank provide for a content of approximately 20 cubic feet for each cubic foot of cold waste fed per minute if a dilution of 40 to one is to be used.

The feed was introduced into the stream passing down the central well through a number of pipes (*F*) extending to a point approximately six inches above the propeller which provided the localized agitation zone desired for the thorough and immediate mixing. The propeller sizes were such that 40 to 50 R. P. M. produced the required circulation. Those familiar with the precipitation of hot saccharate will recognize that because of the scale formed on these feed pipes little heating of the feed occurred while it is passing thru them. The tank discharged continuously by overflowing at the top of the annular space.

The admission of steam was controlled automatically and, with the exception of cleaning the regulator bulb at regular intervals to remove the scale formed thereon, the system required little attention. Obviously, it is desirable to control the rate of feed and this was effectively accomplished by a storage tank from which the cold waste passed thru a set valve to the feed pipes.

As previously indicated, one of the results expected from this apparatus was a precipitate that would settle more rapidly and filter and wash more freely as compared to former products. Tests at several factories had indicated, with the precipitation apparatus used in previous years, settling rates varying from nine inches per hour up to four feet per hour. In experimental work, preliminary to the

design of this apparatus in its present form, rates as high as 20-24 feet per hour were obtained.

The commercial results obtained during the last campaign, in the case of two factories using the new equipment, indicated a settling rate of approximately 10 to 12 feet per hour. Individual tests, made on precipitate formed during periods when a thoroughly satisfactory temperature and feed control were operating, gave results in excess of 15 feet per hour. In the third factory an average settling rate of 7.5 feet per hour was indicated while, in the fourth, the rate was approximately 5.0 feet per hour. At present the cause for the lower figures obtained at the last two of the above is not apparent although it may be a function of feed and temperature control. This increase in settling rate was accompanied by the anticipated improvement in filtration. In the case of the first two factories above mentioned, approximately 66 per cent of the area previously used was required to filter the precipitate from the improved process.

The data included in Table II cover comparative results for a group (No. 1) of three factories which operated old type precipitation plants and a group (No. 2) of four others in which the new system was operated during the 1923-24 campaign. We have also given the results obtained by these groups in 1922-23 before any new installations were made.

TABLE II.

Operating Period.	Apparent Purity of Hot Saccharate Cake. Group I.	Group II.
1922–23 Campaign	86.7%	87.3%
1923–24 Campaign	89.8%	92.5%

The apparent purity of a saccharate cake may be defined as the ratio of polarizing substances to the total dry substance present in a solution resulting from the decomposition of suspended saccharate by means of carbon dioxide, forming insoluble calcium carbonate which is filtered off. In other words this is approximately the apparent purity of the solution which is finally introduced into the crystallization process for the production of granulated sugar.

Where factories are operating on molasses which are similar with respect to the relative quantities of polarizing substances other than sucrose contained, it may be accepted as a relative measure of the ex-

tent of cake washing. Thus the difference between the results obtained by the first group and that by the second group, during the 1923-24 campaign, may be attributed to improved washing of the cake made possible by improved physical characteristics of the precipitate. This difference, amounting to 2.7 per cent in the instance named, would probably increase the amount of granulated sugar recoverable from the precipitate by approximately 5 per cent. A comparison of the second group of factories for the two campaigns 1922-23 and 1923-24 shows a rise of 5.2 per cent in apparent purity but group I also shows a rise of 3.1 per cent. How much of this rise obtained by group I was due to variations in molasses characteristics during the two years and how much to increased superintendance induced by high results being obtained by the neighboring factory is, of course, a debatable question.

As to efforts toward reducing the cost of steam required by the process, space does not permit of a detailed account of the various lines of attack which have been employed. In general, however, these have been directed toward the employment of vapor from one or another of the multiple effect evaporator bodies used in concentrating the beet thin juices. Scaling of heating surfaces, where indirect application has been attempted, is the usual cause for failure. Where direct application was employed scaling and—as we see it now—a lack of control probably caused most of the difficulties. In the apparatus described above most of the heating is accomplished by vapor from the first body of the juice evaporators, which usually operates at approximately 6-8 pounds pressure. This was supplemented by exhaust steam, at approximately 15 pounds pressure, which was automatically introduced when, for any reason, the vapor failed to hold the tank contents at the desired temperature.

In concluding, it may be said that the data incorporated herein present many unfinished aspects. Presentation at this time, however, appeared justified because of the void in the literature relative to the Hot Saccharate Process.

Discussion

President Reese: Gentlemen, the paper is open for discussion.

Mr. Baird: I would like to ask, while in studying you have studied the effect of the composition of the paper itself, upon the

results—the carbonates of ammonia, you know, they sometimes will vary in results, in a practical way, but not in laboratory work.

Mr. Shafor: We have not touched upon that point.

Mr. Baird: It is a possibility, isn't it?

Mr. Shafor: I would say that it is a possibility.

Mr. Baird: I have observed it in one or two instances and I think it is worth while considering.

THE BARIUM PROCESS OF DE-SUGARIZING BEET MOLASSES

By H. W. Dahlberg

Read and discussed at the Denver Meeting, July 15, 1924

In the manufacture of beet sugar, a portion of the sugar contained in the beets is finally obtained, not as pure sugar, but as molasses. Wherever the term "molasses" is used in this paper, "beet molasses" is meant unless cane is specifically mentioned. The amount of sugar lost in this form varies with the amount of non-sugars present in the beets, but is seldom less than fifteen per cent of the sugar introduced. The value of sugar in the form of molasses is only one cent to one and one-half cents per pound and it is therefore natural that many efforts have been made to recover this sugar. A ton of beet molasses contains approximately one thousand pounds of sugar, six hundred pounds of inorganic and organic salts, and four hundred pounds of water. The following is a typical analysis of an American beet molasses:

Brix	86.6
Dry Substance	79.79
True Sugar (Sucrose)	50.21
Ash	13.26
Organic Non-Sugars	16.32

The ash of beet molasses contains approximately:

K_2O	47%
Na_2O	13%
Chlorine	11%
SO_4	11%
CO_2	19%

Potash salts and nitrogenous compounds make up the greater part of the non-sugars.

The principal uses of beet molasses in the United States are as follows:

1. De-sugarizing by the Steffen lime process.
2. Yeast manufacture.
3. Cattle feeding.
4. Alcohol manufacture.

The annual production of molasses in this country is about 300,000 tons, of which I estimate two-thirds to three-fourths is either de-sugarized or converted into yeast. With regard to cattle feeding, I might say that molasses makes an excellent food for cattle, their palates not being so delicate as ours. As some of you may know, beet molasses does not have the pleasant flavor of cane molasses and is therefore entirely unfit for human consumption.

I shall now take up the various processes for de-sugarizing, the most successful being the Steffen Lime, the Strontium and Barium processes. These three metals—lime, strontium and barium—are closely related to each other, and all of them form one or more saccharates with sugar. While many reactions of lime, strontium and barium are similar, we also have some striking differences. As far as we know, lime forms at least three saccharates, strontium forms two, and barium only one, the mono-saccharate. The Steffen process depends upon the formation of the tri-saccharate, the strontium process upon a di-saccharate, and the barium, of course, upon a mono-saccharate. The Steffen process works best at very low temperatures and high dilution of the molasses, the strontium process requires a very high temperature at or near boiling, with a more concentrated molasses, and the barium process gives the best results with a temperature of sixty-five degrees Centigrade, with no dilution of the molasses at all.

The lime process was developed abroad by Steffen and therefore bears his name. Due to many technical difficulties encountered in the early years of the process, it was finally given up almost entirely, so that today there are not over half a dozen factories in Europe using it. The American beet sugar industry, developed largely during the last twenty-five years, was therefore in a position to benefit from European experience. With the aid of the Raymond mill for grinding lime, and labor-saving presses for filtering the saccharate, many of the difficulties were eliminated, so the process has reached a high state of development with us. The Steffen process has one inherent advantage in that lime must be used for the purification of beet juices, and this lime can be applied just as well in the form of lime saccharate as in the form of hydrated lime. The cost of working a ton of molasses by the Steffen process becomes quite low with modern equipment when only a part of the lime used is properly chargeable to it. This gives the Steffen process such an advantage that at the present time it is used

exclusively in American sugar factories, and there are some indications that a number of European plants are again becoming interested in it.

The strontium process was also developed in Germany and France, and is now in active operation at the Dessau refinery in Germany, with several other installations lying idle. In the past when molasses prices were lower it was a very profitable process, but during the war de-sugarizing was prohibited in Germany and since the war molasses prices have been relatively higher than sugar prices, which makes it less attractive. At Dessau the process has been carried to a fine point, the sugar first being recovered as granulated, and the mother liquor containing the non-sugars then subjected to destructive distillation in a carefully worked out process. The nitrogen is recovered in the form of sodium cyanide and ammonium sulphate, and the potash either as fertilizer or refined potassium salts. The fact that Dessau is the only European plant using the strontium process would indicate that under existing conditions it is necessary to combine the recovery of non-sugars with it in order to show a profit. For American conditions it has the disadvantage of high installation costs, excessive use of labor and high strontium costs, and it is rather doubtful if it will ever be adopted in this country.

I have given this brief outline of the two other leading processes before coming to the main topic of this paper—the barium process. This process for the recovery of sugar is based on the reaction between barium hydrate or oxide and sugar, whereby an insoluble mono-saccharate is formed. This reaction has been well known for many years, having been discovered in France by Peligot in 1838. The commercial process was later worked out by two other Frenchmen, Dubrunfaut and Leplay in 1849. The first patents were taken out in this year, and the first installation of the process for working molasses was made at La Villette, near Paris. Three other French factories made experimental installations which were operated for a number of years, but all finally succumbed to high prices for barium sulphate and the high cost of converting the sulphate into the hydrate. Leplay continued working on the process and in 1883–1885 took out new patents for regenerating barium carbonate by roasting in the presence of superheated steam. Even these improvements, however, were not sufficient to make the process a commercial success, and its use in France soon came to an end.

The greatest obstacle to the complete success of the barium process has always been the high cost of the barium hydrate reagent. The source of nearly all barium compounds is barium sulphate, commonly known as barytes, or heavy spar. There are large deposits of barytes in Missouri and Tennessee, and the raw ore is worth about ten dollars per ton. In order to secure barium carbonate, the sulphate, by an old, well-known process, is roasted with coal to form the sulphide, and then carbonated or treated with sodium carbonate to form the carbonate. The net result is that barium carbonate sells in the market for sixty dollars to seventy dollars per ton, while the analogous raw material for the Steffen process, calcium carbonate or limerock, is worth two dollars to five dollars per ton. Otherwise the barium process is so superior to the Steffen process in the way of high purity juices that if the barium reagent could be produced anywhere near as cheaply as lime, the Steffen process would probably soon go into the discard. However, by using the barium carbonate obtained in the process over and over again as the raw material for the barium hydrate required, the final cost is greatly reduced, and it is only by the use of such regeneration processes that the use of barium becomes feasible. By this procedure, only the small losses of barium carbonate occurring in several steps of the process need be made up from day to day, with fresh barium carbonate made from the sulphate.

A great many patents have been taken out for processes claiming to give a cheap conversion of barium sulphate or carbonate into the oxide, but most of these have been complete failures and it is not necessary to describe them here. I shall confine myself to a description of those methods which give promise of commercial success. An interesting process which has been brought out during the last few years is that which is known as the DeGuide process. It has been patented by the inventor, M. DeGuide, a Belgian, and very strong claims are made for it, but as yet it is still in the experimental stage. The process depends on the formation of barium silicate, presumably in the form of tri-barium silicate, by burning barium carbonate and silica together in a cement kiln. This forms a clinker very similar to cement clinker, which is then ground to one hundred mesh and treated with hot water. The reaction between barium cabonate and finely powdered silica takes place between twelve hundred and fifty degrees and twelve hundred

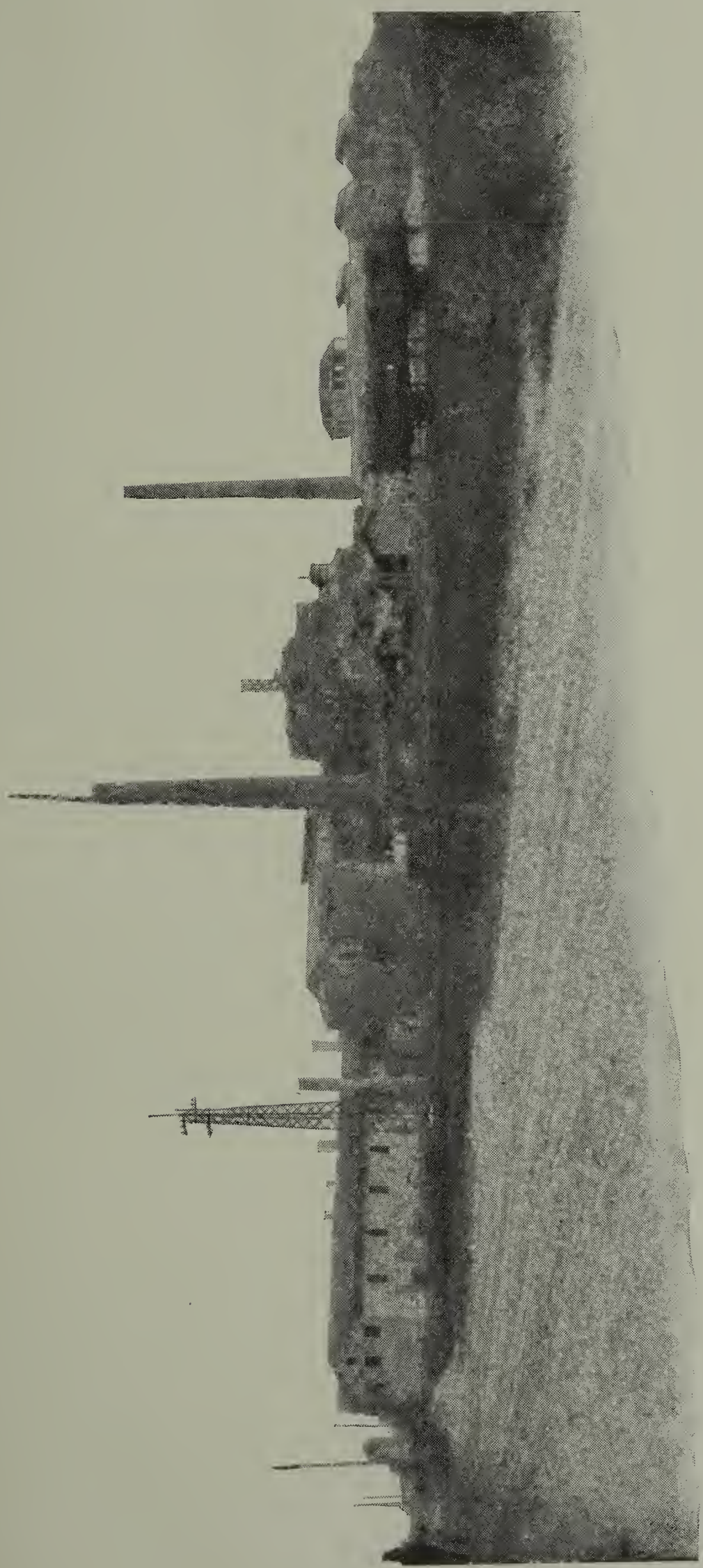


FIG. 1. An Italian Beet-Sugar Plant Employing the Barium Process.

and seventy degrees Centigrade, and it is claimed that the material is very friable and that it can be pulverized quite cheaply. It is asserted that the clinker gives a yield of forty per cent BaO in the form of hydrate, and the remaining insoluble mono-barium silicate can be mixed with more barium carbonate and burned to a new clinker. The barium carbonate is thus utilized repeatedly with only small losses of barium. The process sounds very interesting and if the claims of its owners can be substantiated in practice, will undoubtedly prove of value. It is to be hoped that a commercial installation will soon be made and demonstrate whether the conversion can be made as cheaply as is hoped. Some of the difficulties which may be anticipated are: (1) The kiln lining tending to fuse with the charge, and (2) Contamination of the clinker with inorganic salts from molasses.

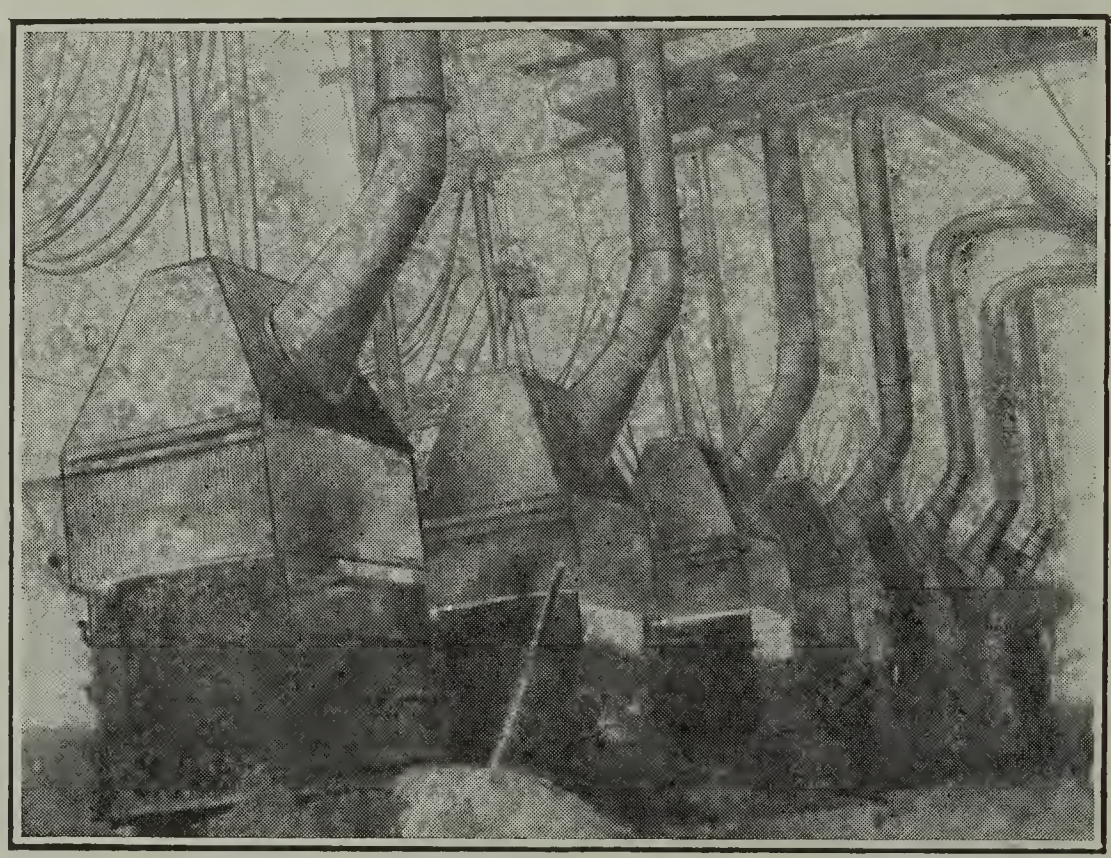


FIG. 2. Electric Furnaces in an Italian Beet-Sugar Plant. These are used for Converting Barium Carbonate to Barium Oxide.

As far as I have been able to discover the only countries in the world where the barium process is now used for the treatment of beet molasses are Italy and Canada. At some time in the nineties the process was developed in Italy, the method of regeneration of barium carbonate being reduction with coal in a reverberatory furnace. About 1901 conversion of the barium carbonate into oxide by means of the electric furnace was developed and this method

is the one in use today. I had the opportunity of seeing this process in operation and it is working quite successfully under Italian conditions, where the cost of power is from two to five mills per kilowatt hour and the cost of common labor is eighteen lire per day (about eighty-five cents at current rate of exchange). The furnace used is quite simple, using two arcs in series, A.C. current at fifty volts, and with no refractory lining. The amount of hand labor required for charging the furnaces and separating the barium oxide core from the unconverted material is very excessive. The dust problem in the furnace room is a very serious one and the working conditions would be considered rather bad in the United States. The cost of conversion consists chiefly of the three large items—power, electrodes, and labor.

The core of barium oxide obtained from the furnace is crushed and slacked with hot water in a tank provided with stirrers. A solution of barium hydrate of a density of thirty-nine degrees Be. is obtained, and this solution, after most of the insoluble matter has been settled out, is ready for the precipitation of sugar. The settling is done in a series of tanks, called hydrators, and about once a week the sediment at the bottom of the tank is leached several times with boiling water and then run to a filter press, where it is washed as free as possible of soluble barium. As you will notice, this part of the installation is rather crude and could be greatly improved in a new plant, but I am describing the equipment now in use.

The barium hydrate solution having been obtained, it is run to a storage tank and from there to a compartment trough above the precipitation tubs. Ten of these compartments are filled to a certain volume with the hydrate solution at a temperature of eighty degrees, and ten other compartments with molasses at about thirty-six degrees. The hydrate solution is run into the precipitation tub first, and followed immediately by the molasses; after a slow stirring by hand for about a minute the reaction is complete, and the tub is nearly full of solid, coarse-grained saccharate, which looks and feels very much like sea sand. The operation of this station is very simple and rapid, the tubs serving both for precipitation and filtration. Near the bottom of each tub is a twenty-two-mesh iron screen, laid in loose with a rubber gasket around the edge. About two ordinary bucketsfull of cloudy mother liquor or waste water is caught when the valve at the bottom of the tub

is first opened, and this is poured back on top. The waste water then runs clear, and after this has drained off for a short time, the washing with a hot solution of two per cent barium hydrate begins. The first washing is done by wash water which has been used once before in a previous washing, and is followed with fresh wash water. Each tub handles eight hundred pounds of molasses at a time, and there being ten tubs, it takes fourteen cycles in twenty-four hours to handle fifty-six tons of molasses. It takes four men per shift to run the entire station, including the measuring of hydrate and molasses, the precipitating, filtering, washing and dumping.

The dumping is done by tipping the tub by means of a hand wheel and gear. Nearly all of the saccharate slides out immediately, and the remainder is flushed out with a hose, using sweet water. The temperature of the saccharate is held at about sixty-five degrees Centigrade throughout the filtration and washing period. This is done without any difficulty by keeping the wash water at about seventy degrees Centigrade.

The saccharate is scrolled to a saccharate milk tank, and from there goes to juice carbonation. The mixed waste and wash water is pumped to waste water carbonation, one man handling all of the carbonating. From the saccharate a white $BaCO_3$ is obtained, and from the waste water a yellow or brown carbonate. The two types of $BaCO_3$ cake, one from the juice and one from the waste water, are filtered and washed in ordinary plate and frame presses. The waste water carbonate is always of poorer quality than the other and is therefore dried separately. The dried carbonate is then ready to be converted into the oxide again, after being mixed with about four and one-half per cent pulverized coke.

The sugar juice obtained from the carbonation of the barium saccharate is of very high purity, about 96, and the production of white granulated sugar from it offers no technical difficulties.

The barium oxide obtained from the white carbonate tests eighty-eight to ninety-two per cent BaO, while that from the brown carbonate tests considerably lower. The impurities are barium carbide, barium sulphide and some unconverted $BaCO_3$. The insoluble impurities gradually accumulate in the sediment formed in the bottom of the settling tanks or hydrators, and when this sediment gets as low as fifty per cent $BaCO_3$ by analysis, it is finally washed as thoroughly as possible and then discarded.

In order to be successful in the United States, the Italian process would have to be worked under the following conditions:

1. Large margin between the cost of molasses and sugar.
2. A tonnage of molasses sufficiently large to operate a plant the year around.
3. A plant with labor-saving equipment developed to the last degree.
4. Utilization of the non-sugars in the form of marketable by-products.

In conclusion, I wish to emphasize again that the success of any barium process for the recovery of sugar from molasses rests above all upon the cheap regeneration of barium oxide, and it is to

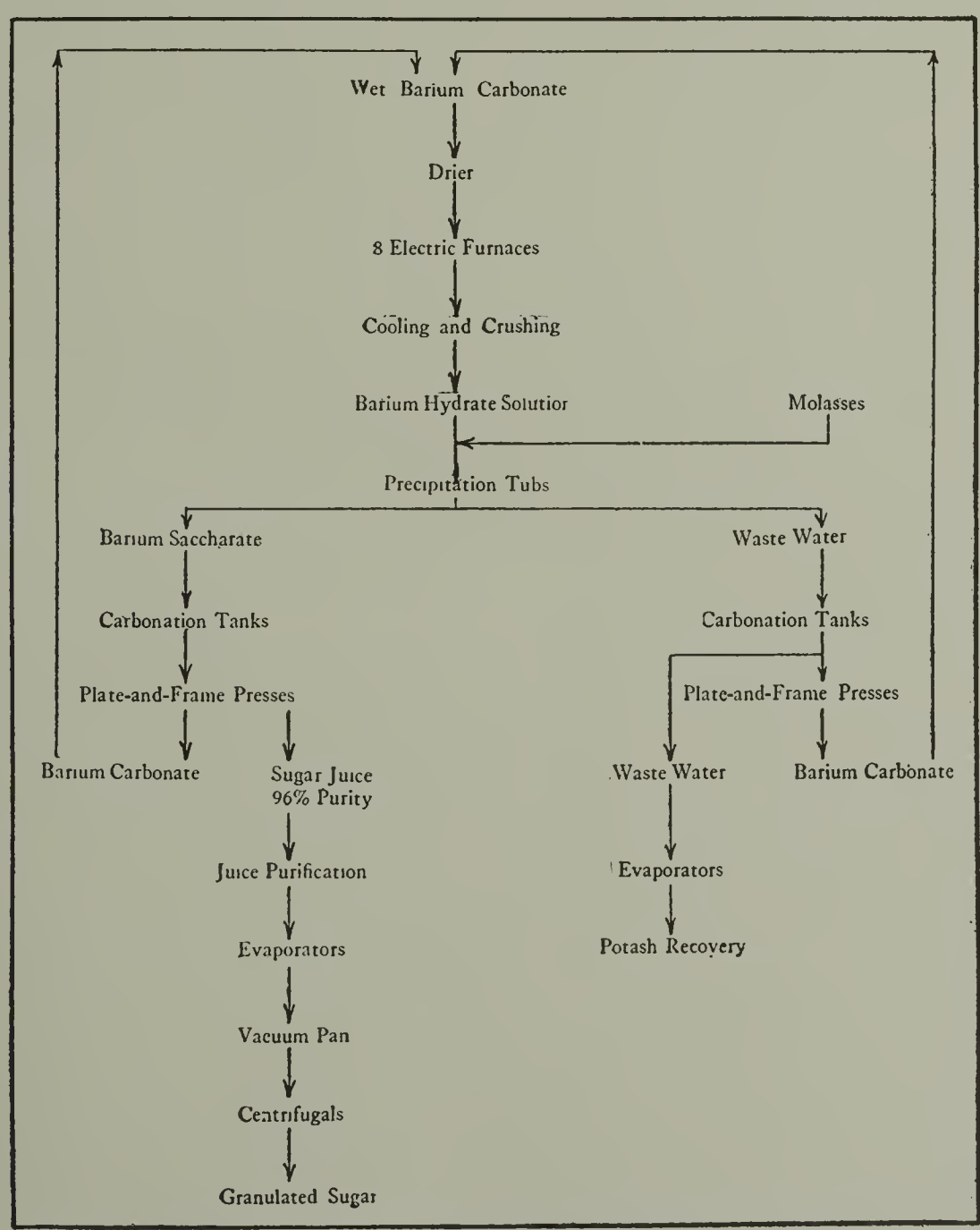


FIG. 3. Flow Sheet of Italian Barium Process.

be hoped that the interest which is now being taken both here and abroad in the utilization of molasses will result in the development of better processes for making barium oxide or hydrate.

Discussion

Dr. John C. Olsen: Are they using arc furnaces?

Mr. Dahlberg: Yes, with two arcs. They have automatic regulation of electrodes but, in many ways, the installation is not as modern and up-to-date as American electric furnace installations.

Dr. Olsen: What is the capacity of this plant?

Mr. Dahlberg: The capacity is about sixty tons of molasses per day. Each furnace produces a block or core of barium oxide of about two thousand pounds.

Dr. Olsen: At one charge?

Mr. Dahlberg: At one charge; but that, however, is only about one-fourth of the total charge. This is merely an estimation.

Dr. Olsen: The other three-fourths goes on?

Mr. Dahlberg: The other three-fourths is largely unconverted material and goes through the furnace again.

Dr. Olsen: Do you know the length of time of furnacing?

Mr. Dahlberg: From fifteen to twenty-four hours. The consumption of electric power per ton of barium oxide is quite high.

Mr. Bailar: Can you use that mixture of barium hydrate and barium sulph-hydrate without changing it into carbonate first?

Mr. Dahlberg: It can be used directly for precipitation, but most of them prefer to carbonate first.

President Reese: Are there any further questions, gentlemen?

Prof. Alfred H. White: Mr. Dahlberg said there are no technical difficulties in producing sugar from the saccharate; so I suppose there is no danger from poison, which is referred to in the literature. Is there any danger of poison from the barium?

Mr. Dahlberg: That is handled in this way: First, the barium carbonate is precipitated by carbon dioxide gas, careful attention being paid not to form any bicarbonates. The very last traces of barium are removed, either with a soluble sulphate or sodium carbonate. We, ourselves, have produced sugar in this way and tested it by the most delicate spectroscopic tests and found no trace of barium. We also have the evidence that sugar has been produced in Italy, and other countries, for over twenty years, by the use of this process.

The barium process is better than the Steffens process in one respect. The barium process produces waste water of fifteen to twenty per cent dry substance, while the Steffens process produces a waste of less than half a per cent of dry substance, so that, with the former, it becomes possible to evaporate and recover by-products.

Dr. A. N. Bennett: I would like to ask if this plant is working the year round, or just during the sugar campaign?

Mr. Dahlberg: It has worked at least eight months out of the year, in the past, and, with their new installation, will probably work the year round.

DISPOSAL OF WASTE FROM BEET SUGAR INDUSTRY

By EDWARD BARTOW

Read and discussed at the Denver Meeting, July 15, 1924

Waste from a beet sugar factory like that from other organic chemical industries dealing with carbohydrates contains large amounts of putrefactive organic matter both in suspension and solution. Factories located on large streams dispose of this waste easily by dilution. Factories not located on large streams have difficulties because the concentrated organic waste removes the oxygen from the water and causes trouble. Fish are killed and the stream becomes unpleasant. Much effort has been expended to prevent this trouble and also to make an economic use of the waste.

Waste from a sugar factory may be classified in four parts: (1) Beet washing water, (2) Battery water, (3) Lime waste, (4) Steffens waste. In a plant of approximately 1000 tons daily capacity, there will be about 4,000,000 gallons of beet washing water, 600,000 gallons of battery water, 150,000 gallons of lime waste, and 250,000 gallons of Steffen's waste.

1. The beet washing water used for carrying and washing the beets contains dissolved organic matter and considerable suspended matter, consisting of mud, pieces of beets, and beet tops. The pieces of beets and beet tops can be removed by screens, and mud will settle quickly in a pond or in a stream. The beet washing water has low oxygen consuming power compared with that of the other wastes and should have less deleterious action on a stream. In cases where the stream flow is very low, it would be inadvisable to try to pond all of it during extreme dry weather as users of water down stream would be short of water.

2. The battery water including the water from the pulp presses contains fine particles of pulp in suspension and organic soluble matter, both of which are putrescible. The pieces of pulp can be removed by fine screens, and the water treated with lime and then with carbon dioxide, the precipitate removed and the water returned to the process.

Pearse and Greeley[1] operated an experimental disposal plant at the Decatur, Indiana factory of the Holland-St. Louis Sugar Company. The tests were run on the crude waste from the diffusion batteries and the pulp presses. They used a screen, settling tanks, sludge beds, sprinkling filters, sand filters, and an arrangement for dosing with lime. They summarized their results as follows: fine screenings and sedimentation are indicated as necessary for any type of treatment plant. The effluent of the settling tanks can be treated on sprinkling filters at a rate of about 200,000 gallons per acre per 24 hours, and sand filters at the rate of about 75,000 gallons per acre per 24 hours. Should the concentrated sewage be mixed with an equal volume of beet carrying water, the data indicate that a settled effluent could be treated on sand filters at a rate of 100,000 gallons per acre per 24 hours. It would have been desirable to make further tests with a mixture of the diffusion battery and pulp press waste and an equal valume of beet carrying water. These rates of filtration result in quite costly installations and every effort should be made to keep the cost down by utilizing local conditions of stream flow and soil to the utmost.

Following these experiments which indicate that construction of tanks and sprinkling filters or sand filters would be very expensive, a fine screen was installed, the liquid treated with lime, the lime precipitate removed, and the supernatant liquid used in the process. As far as I know, no record has thus far appeared in the literature of the results of this experiment.

In the discussion of the paper by Pearse and Greely, Mr. W. H. Dittoe, chief engineer, Ohio State Department of Health, tells of the construction of a disposal plant at Paulding, Ohio. There was constructed a screen to remove coarse suspended matter. The screen effluent is treated with an average of thirteen grains per gallon of lime and two grains per gallon of iron. After which it was pumped to basins having a detention period of 3.8 days. One-third of the flow is returned to the water supply for transporting beets, the remaining two-thirds is mixed with the flow from a basin containing the Steffen's waste and lime cake, and passed to a settling basin having a twenty-two hour detention before discharging into the creek. While the effluent from the final basin was dark in color, the addition of this effluent to the stream caused no complaint to the State Department of Health.

[1] *Am. J. of Pub. Health*, 10, 312–23 (1920).

It is Mr. Dittoe's conclusion that oxidizing processes, which would be required for a more complete treatment, would require a large expenditure. Such expenditure does not seem to be justified unless it should be shown that public health is involved or that the rights of riparian owners demand more complete treatment.

In further discussion of this article, Mr. Robert Spurr Weston discusses the chemical and bacteriological action which occurs in the disposal of certain wastes from what might be called the carbohydrate industries. From his own experience and that of George W. Fuller with waste from cane sugar plants and in plants for the manufacture of butter substitutes, he concludes that there are three means of purification to be tried out in such cases; yeast treatment to remove sugar, activation to effect the destruction of the organic matter, and lime treatment to correct acidity which interferes with subsequent treatment.

It was our own opinion that parts of the organic soluble matter might be removed by fermentation in ponds, and an attempt to do this has been tried and will be described later in this paper.

3. The lime sludge waste contains for the most part calcium carbonate precipitated from the Steffen's waste, and mixed with enough water so that it can be pumped. The calcium carbonate will settle readily but the supernatant liquid contains organic solubles, and, when neutralized, will be putrescible. It may be possible to use the excess of alkali to partially neutralize the acids formed by putrefaction of the battery water.

4. The Steffen's waste consists of the molasses from which the sugar as tricalciumsaccharate has been removed by precipitation with lime. It amounts to approximately 300 cubic feet for each ton of molasses. This material contains practically no suspended matter and is very rich in organic soluble matter. The oxygen consuming capacity is very high, about 3,000 parts per million, so that when added to water in a stream unless suitably diluted, it absorbs the dissolved oxygen making it impossible for fish to live in the stream.

A summary of technical methods proposed for the utilization of molasses has recently been published by the Bureau of Standards.[2] The Bureau has made a thorough search of patent literature, American, English, French, and German, and has given a thorough resumé of the patent literature on the subject. It states:

[2] Circular of Bureau of Standards, No. 145 (1924).

"The molasses contains numerous valuable substances which have never been successfully recovered outside of Germany. For many years that country has seen fit to veil its developments and discoveries, and to maintain the strictest secrecy regarding the operation of its molasses plants. The scientific literature on the subject is practically barren, so far as the actual results achieved in Germany are concerned."

The investigators of the bureau have uncovered over 1,000 German patents on molasses utilization and associated subjects. These patents were not listed under sugar or molasses, but were concealed under other subjects. This statement illustrates the difficulty of treating the molasses and disposal of the wastes obtained therefrom. The American beet sugar industry has therefore a difficult and serious problem to solve.

The reviews of the patents show possible methods of treating the Steffen's waste, but the literature gives no report of the results obtained, and it will be necessary for the American industry to do considerable research work in order to solve its problems. The patents indicate that the waste molasses aside from its use in the recovery of sugar by the Steffen's process, may be used as a fertilizer, a cattle food, a source of alcohol, a medium for the production of yeast, a fuel, a filler in many manufactured products, a source of potash, and various valuable organic and inorganic chemicals.

The patent literature reviewed by the Bureau of Standards indicates the possible recovery of the following: "Methylamines, ammonia or ammonium sulphate, sodium or potassium cyanides, nitrogen bodies, such as betaine and glutaminic acid, alkali salts (K_2CO_3, Na_2CO_3, K_2SO_4) vegetable carbon and tar, and various minor products, such as methyl alcohol, glycerin, organic acids, and esters. These latter have received considerable attention in the patent literature because of their production from distillery slop or vinasses." For further information those interested are referred to the report of the Bureau of Standards.

In America, most of the molasses is treated by the Steffen's process or other saccharine processes to recover the maximum amount of sugar. No record has been found of the recovery of organic values other than the sugar. At Decatur, Indiana, the waste was concentrated and incinerated and potash salts recovered. The expense of the treatment was probably as great or greater than value of the products recovered. Part of the expense may

be charged to waste disposal. Since the Germans practice the successful recovery of both inorganic and organic values from the waste, it is to be hoped that a similar process may be developed as an aid to the industry in the United States. The usual practice for the disposal of Steffen's waste in America is dilution in streams.

The factory of the Northern Sugar Corporation at Mason City, Iowa, is located on a small stream. At times the entire flow of the stream is used at the factory. In order to take care of the waste, it will be necessary to obtain more water for dilution or to provide for ample treatment of all the waste with little or no dilution. More water could be obtained by sinking a well for wells in the vicinity, at the city water works and the packing plant, gave promise of a yield of approximately one million gallons a day from a well 20 inches at the top, 12 inches at the bottom, and 1300 feet deep. This well will be available for the 1924 season and will increase the available water for treatment.

The expense of tanks and sprinkling filters, or sand beds, if sand had been available, did not seem to be warranted. Preliminary experiments with ponds promised some success by settling and fermentation. Ponds sufficient to store all of the Steffen's waste and to give 22½ days detention period for the waste water from the diffusers and the feed presses were constructed on a plot of land near the factory.

Treatment was carried on approximately as follows: (1) Beet washing water was screened and passed through a small pond to the creek. (2) The battery water amounting to 600,000 gallons daily or approximately 80,000 cubic feet was passed through four ponds; numbers 1, 2, and 3; each four acres in area and each calculated to give a detention period of 4.6 days to the waste. Number 4, six acres in area, calculated to give 8.6 days detention or 22.4 days in all. The waste was pumped to the highest point on the land and flowed through the ponds by gravity. It entered each pond at the shallowest part and passed out over spillways at the deepest part. The waste was aerated by passage over riffles at the spillways from ponds Nos. 1, 2, and 3. (3) A pond 1000 feet by 200 feet and 4 feet deep was provided for the lime sludge. This pond was so situated that the overflow could be passed to ponds Nos. 2, 3, or 4, and by neutralizing the acids formed by fermentation assist in the purification process. (4) A pond fourteen and one-half acres in area was provided for the Steffen's waste. This should

have had capacity sufficient to contain the Steffen's waste for the whole season without allowance for seepage or evaporation. Owing to fear that the embankments would not hold, it was found necessary to remove some of this waste into pond 2 before the close of the season.

Samples of the waste and samples of the effluent from the ponds were taken throughout the campaign. Owing to the necessity of disposing of the Steffen's through the ponds provided for the battery waste, the purification during the latter part of the campaign was not entirely satisfactory. The campaign started October 1 and it required 25 days to fill the ponds (calculated 22.5). The purification shown by the samples taken on November 5 measured in terms of reduction of dissolved residue was 64 per cent, and in terms of oxygen consumed, 62 per cent, in the first pond, and there was but little further removal in the following ponds. Treatment with lime or mixing with the lime sludge after the first pond, would, we believe, increase the efficiency of the plant.

The suspended matter was practically eliminated. The remainder of the Steffen's waste was allowed to flow into the stream during a period of high water and caused no complaint. About the close of the campaign, under conditions of cold weather when the river was frozen and but little water flowing, large numbers of fish were killed in the stream several miles below the plant.

For the coming season the embankments around the Steffen's waste pond have been strengthened and the pond deepened, and it is expected that it may be possible to store all the waste until a period of high water arrives.

An attempt is being made to utilize the experience of others in treating these organic wastes to obtain the valuable compounds described in the earlier part of the paper. Some of the Steffen's waste has been concentrated and when evaporated with superphosphate of calcium in the proportion of 8 of concentrated Steffen's to 6, 7, or 8 of the superphosphate, and 6, 7, or 8 of water, the product was obtained which is apparently quite stable and which might be used as a fertilizer. The drying of the mixture has been accomplished in a spray dryer. If a larger proportion of the concentrated Steffen's waste is used, a sticky deliquescent substance is obtained. Attempts to dry the Steffen's alone in the dryer give a sticky product. The phosphate, the nitrate, and the potash should all be available for a fertilizer.

The waste can be dried in a vacuum dryer to the consistency of molasses candy. It is very deliquescent and takes on moisture when an attempt is made to grind it. Solvents may help to separate the constituents.

At a later time it is expected that some more positive results can be given.

Discussion

President Reese: Gentlemen, we have time for discussion. Are there any questions any of you would like to ask Dr. Bartow? It is a very interesting paper and I am sure that we, in this country, should be able to recover the valuable products of our beet sugar waste as they do in Germany. I don't think it is an impossibility. We have done it with dyes and we can do it with sugar waste.

TECHNICAL ACCOUNTING IN THE SUGAR INDUSTRY

A Highly Developed System of Accounting has been One of the Principal Factors Responsible for High Production Efficiencies and Close Operating Control.

By H. E. ZITKOWSKI

Read and discussed at the Denver Meeting, July 15–18, 1924

It is perhaps presumptuous to emphasize the importance of technical accounting before this body, for chemical engineers concern themselves, not only with the "how," but also with the "how much," of their problems.

During the infancy of the development of a technical problem, the qualitative phases demand and deserve greatest attention, but unless the quantitative phases of the problem are given equal, or even greater care, the life expectancy of the problem will classify it as a poor risk in the business mortality tables. This is as it should be.

It is but in the nature of things that the sugar industry, owing to its age, its comparatively standardized processes and keen, world-wide competition should have developed its quantitative technical accounting methods to a greater degree of refinement than most similar industries. Furthermore, it is well to emphasize, that while competition is keen, a wider, freer exchange of comparative technical —not financial—operating data exists among the hundreds of sugar producers than among any similar group of enterprises.

Adds Stability to Industry

More than thirty years ago a comparative operating control was instituted by a large number of Belgium, Dutch and German sugar manufacturers. This was directed by a competent engineer, with headquarters in Brussels, to whom all reports were sent, who reduced the data to comparable units, edited, compiled and published them for distribution. Each plant was given a key letter, and

each member of the association received complete data covering the entire group. Similar cooperative bureaus were established between French and Russian producers and also in the cane sugar producing countries. Perhaps the most elaborate system of this nature now in existence, is among the large group of Javanese sugar producers. Their mutual reports cover even the minutest details of operation having possible influence on the final results. That such data is invaluable to the sugar technician, operating under fairly similar conditions, is obvious. And how has this expressed itself in the market level of the product, sugar? Excepting the period during and since the World War and the temporary fluctuations occassioned by world wide crop failure, the price of sugar definitely tends downward as Table I. indicates.

TABLE I

WHOLESALE PRICES OF SUGAR, 1870–1913.

Year	N. Y. Wholesale Price of Granulated Sugar
1870	13.53 cents per pound
1880	9.60 cents per pound
1890	6.17 cents per pound
1900	5.32 cents per pound
1910	4.97 cents per pound
1913	4.28 cents per pound

In the spring of 1914, just before the outbreak of the war, the price actually decreased below 4 c. per lb. Duty-free raw sugars, of about 96 deg. purity, in the primary markets at that time, were selling in the neighborhood of 2 c. per lb.

If it is now considered that this total price includes the very considerable item of the cost of raw material, the costs of transportation, all costs of materials and labor in the process of manufacture, as well as all overhead and profit, the fact will be appreciated that when comparing costs and efficiencies of operations the sugar producer must reckon his costs not in cents per pound, nor even in mills per pound, but in tenths of mills per pound. On the other hand, owing to the volume of production, even at the rate of tenths of mills per pound, the totals assume considerable proportions. The larger of the beet-sugar companies in this country will produce perhaps 600,000,000 lb. annually and a difference of one tenth of a mill per pound amounts to $60,000. So the extensive technical control in use has been developed more or less of necessity.

Daily Report, Final Criterion of Operation

A typical American factory superintendent's Daily Operating Report is shown herewith. In form, these reports will vary more or less between the different sugar companies, though in substance, practically the same data all compiled by all. This is the final criterion of the technical operating results and is compiled and calculated from literally dozens of various agricultural, factory station, laboratory and supply warehouse reports, to go into the detail of which would be entirely beyond the scope of any one paper. Each item on this report is a problem in itself.

Consider for a moment the first item on this report "Beets Received." The plant in which the report, here being considered, originated, pays the grower of beets on a basis of the sugar content of the beets delivered by him, with the result that each load, as delivered, is sampled, and occasionally as many as 1,000 samples per day are received for analysis. The problem here begins with the proper and correct sampling of the load. Individual beets vary widely in sugar content, even though they were neighbors in the field, so that it becomes a real problem to obtain a representative sample under all conditions. Sugar is not uniformly distributed in the beet itself, so that a further problem is involved in obtaining an aliquot portion from each beet in the sample for analysis. The most practical and efficient method of determining the sugar content in beets, under all conditions, is still a subject for discussion, although it is prescribed by law in at least one state.

Similar problems arise with each of the other items on the report involving sampling, analyses, weight and measurements. It is worthwhile to discuss, for a moment, the subject of sampling the many dozen of products or stages of the intermediary steps in the process of manufacture. The probability of error creeping into the results, due to incorrect sampling, wilful or otherwise, is greater than is the case with most products; yet chemists will devote greater attention to the details of analysis, than to the methods of obtaining their samples for analysis, with the result that, say in the matter of the determined losses, a beautiful record is established and the unaccountable losses are equally as great as those accounted for.

"The Human Element in the Mill," so ably discussed by H. K. Moore in a paper before the Institute some years ago, is perhaps the most important factor to consider in the matter of sampling. The

REPORT I.

DAILY OPERATING REPORT

B Factory, 87th Day, from 6 A.M. Oct. 28 to 6 A.M. Oct. 29, 1920

Tons	Last 24 Hrs.	To Date	Daily Ave.
Beets Received	655	226099	2600
Beets Sliced	1691.605	222103.709	2552.9
Bags Sugar	7585	802447	9227
Bags Dried Pulp	2038	224224	
Bags Mol. Pulp		38831	
Total Bags Pulp		263055	3024
Tons Crude Potash	8.310	1089.166	12.52

	Last 24 Hrs. % Sugar	Last 24 Hrs. Purity	Last 24 Hrs. % Tare	To Date % Sugar	To Date Purity	To Date % Tare	Days Yet To Operate
Beets Received	19.42	81.2	3.95	18.82	80.6	3.80	
Beets Sliced	18.68	80.7	—	18.76	80.4	—	4

		Last 24 Hrs. Total Tons	Last 24 Hrs. % On Beets	Last 24 Hrs. % On Sug. Entered	To Date Total Tons	To Date % On Beets	To Date % On Sug. Entered
1	Total Sugar Entered	315 992	18.68	100.00	41671.118	18.76	100.00
2	Sugar in Pulp	1.692	.10	.54	247.831	.11	.59
3	Sugar in Waste Water	.677	.04	.21	87.945	.04	.21
4	Sugar in Lime Cake	2.768	.16	.87	199.942	.09	.48
5	Sugar in Steffen Waste Water From	4.704	.28	1.49	332.186	.15	.80
6	Total Known Losses	9.831	.58	3.11	867.904	.39	2.08
7	Sugar Bagged	379.250	22.42	120.08	40122.350	18.07	96.28
8	Sugar Estimated in Process (Gran. Eqv.)				100.000	.05	.24
9	Sugar Melted Bght. or From Prev. Camp. (Gran. Eqv.)				89.826	.04	.22
10	Net Extraction				40132.524	18.08	96.30
	Molasses Statement						
11	Sugar in Molasses Produced	135.087	7.98	42.76	10832.217	4.88	26.00
12	Sugar in Molasses Worked in Steffen	135.087	7.98	42.76	10832.217	4.88	26.00
13	Total Sugar in Mols. to Pulp Plant				236.942	.11	.57
14	Wet Molasses Produced	257.800	15.24	81.57	21315.800	9.60	51.18
15	Wet Molasses Worked in Steffen	257.800	15.24	81.57	21315.800	9.60	51.18
16	Total Wet Molasses to Pulp Plant				442.658	.20	1.06
17	Steffen Extraction (12-5 in % of 12)		96.57%			96.93%	
18	Steffen Waste Produced % Wet Molasses Worked	2240–869%			197501–926%		

REPORT I—*Continued*

				Last 24 Hrs.			To Date		
				Total Tons	% On Beets	% On Sug. Entered	Total Tons	% On Beets	% On S Entered
	Pulp Statement								
19	Dried Pulp Bagged			101.900	6.02	32.24	11211.200	5.04	26.90
20	Molasses Pulp Bagged % Mol. Day To Date						1941.550	.87	4.66
21	Total Pulp Bagged						13152.750	5.91	31.56
22	Lbs. Fuel Oil to 100 Lbs. Dried Pulp Produced				35.5			38.0	
	Material Statement					% On Sug. Ext'd			% On Sug. Ext'd
23	Lime Entered in Carbonations (Slacked and Powder)			129.798	7.67	34.22	11507.197	5.18	28.68
24	Total Lime Used			129.798	7.67	34.22	11507.197	5.18	28.68
25	Lime Entering Coolers to 100 Sug. in Mols. Worked			129.798	96.1%		11038.048	101.9%	
26	Vertical Lime Produced			126.408	7.47	33.33	10152.945	4.57	25.29
27	Vertical Waste % Vertical Prod.						100.806	.99%	
28	Rotary Lime Produced from Lime Cake			20.741	1.23	5.47	1752.689	.79	4.37
29	Spall Lime Produced from Spalls			15.001	.89	3.98	639.647	.29	1.59
30	Rotary Lime Used % Total Lime Used			20.741	15.99%		1752.689	15.24%	
31	Spall Lime Used % Total Lime Used			15.101	11.64%		639.647	5.56%	
	Fuel Oil	*Last 24 Hrs.*	*To Date*						
32	B. H. Factory	1397.3 Bbls.	125993.0 Bbls.	227.421	13.45	81.44	20505.474	9.24	51.10
33	B. H. Potash Mfr.	153.2	16190.0	24.933	1.47	6.57	2664.958	1.20	6.64
34	B. H. Total	1550.5	142183.0	252.354	14.92	8.01	23170.432	10.44	57.74
35	Pulp Plant	228.8	31591.8	36.150	2.14	9.53	4993.027	2.25	12.45
36	Rotary Kilns	60.2	5005.4	9.798	.58	2.58	814.040	.37	2.03
37	Spall Kiln	32.2	1353.3	5.240	.31	1.38	220.791	.10	.55
38	Total Fuel Used	1871.7	180133.8	303.542	17.95	101.50	29198.290	13.16	72.77

REPORT I—*Continued*

		Last 24 Hrs.			To Date		
		Total Tons	% On Beets	% On Sug. Entered	Total Tons	% On Beets	% On Sug. Entered
	Fuel Oil *Last 24 Hrs.* *To Date*						
39	Cold Water 14 Million Gals. 1253		3452 %			2353 %	
40	Boiler Feed Water	3944.5	233.1		345656.0	155.7	
41	Lime Rock	202.450	11.97	53.39	18333.800	8.26	45.68
42	Lime Rock as Spalls	28.510	1.69	7.52	1227.500	.55	3.06
43	Coke	23.980	1.42	6.32	2110.935	.95	5.26
44	Sulfur	.887	.05	.23	80.239	.04	.20
45	Soda to Juices	4.850	.29	1.28	423.400	.19	.06
46	Total Soda Used	5.100	.30	1.35	449.493	.20	1.12
47	Kieselguhr	1.222	.07	.32	110.215	.05	.27
48	Wash Water Used on Carbonation Filters	910	*% On Cake*	109	94737	*% On Cake*	148
49	Wash Water Used on Cold Sacch. Filters		*% On Cake*			*% On Cake*	

	Diffusion Batteries						Pans													
							Last 24 Hours							To Date						
	No. in oper.	No. Cells in Circ.	Tons per Cell	Per cent dll	Pr. Ct. draft by wt.	Time of di$.	Qual.	No.	App. Purity Fill-mass	App. Purity Green	Total Drop	Theo. Yield	Hrs. Cryst.	No.	App. Purity Fill-mass	App. Purity Green	Total Drop	Theo. Yield	Hrs. in Crys.	Cu. Ft. Fillm. T. Beet
Today . . .	2	20	6.1	54	150	1° 44′	Str.	10	84.2	70.2	14	56	—	1076	84.1	71	13.1	54	—	12.02
To Date .			6.1	54	158	1° 36′	Raw	9	72.4	56.1	16.3	51	32	507	71.5	55.2	16.3	51	44	3.24

Battery Extraction; Sugar in Diff. Juice To-day 312 Tons 98.1 Per cent on Sug. Ent. 41296 To Date 99.1 Per cent on Sug. Entered

Temperature; Bat. Max. 80°C Ave. Before Lime 90°C Before 1st Filter 90°C Before 1st Refilter 93°C
Before 2nd Filter 101°C Finished Cooler 16°C Hot Sacch. 86°C Leaving Thickener 84

superintendent in charge establishes certain permissible limits, as an illustration, for the loss of sugar in the pulp and when there are variations from these limits, he expresses himself, often not too gently. The operators of the diffusion battery, like most of us, prefer to avoid trouble, and if experienced, often know before analysis is made that the pulp will be high, although the cause may not be within their control. The result is often a doctored or salted sample, and as a consequence large unaccounted losses at stock-taking periods. But even so, very gratifying progress has been made in this direction. It was not so many years ago that superintendents rated the value of some of their foremen and workmen, on the basis of their ability to "put it over" on the laboratory; happily that day is practically past.

Referring again to the report it will be observed that this gives the quantities of the various products and materials of importance in the process, both for the last operating day, and to date, expressed in terms of per cent on beets and in terms of per cent on sugar entered. Thus it presents a comprehensive and continuous picture of the operating results. With this before him, and comparing these results daily with results obtained in previous years, or at other plants, the superintendent can readily determine the weaknesses of his operations and can concentrate on these.

Improving Operating Efficiency

That these efforts, striving for increased operating efficiency, although slowly, have in the course of time resulted in very definite results, may be gathered from the data presented in Table II.

Factory A refers to one of the pioneer plants of the country, and although now it is one of the smallest, at the time of its erection it was hailed throughout the country as a mammoth new beet sugar factory, destined to revolutionize the agricultural and business conditions of the West. It did play an important part. It served as a training school for several score of men, who, eight to ten years later, when the active development of the American beet sugar industry took place, were prominent in the operation of new plants. Factory A, owing to its small size, age and location in a territory not favored with an average quality of beets, is not one of the most efficient in the country, and the data are not given in that light, but rather as being of historical interest.

TABLE II.

COMPARATIVE SLICING CAPACITY AND SUGAR EXTRACTION IN TWO PLANTS OVER A PERIOD OF 33 YEARS

Year	Factory "A"		Factory "B"	
	Average Daily Slicing in Tons	Average Extraction of Sugar in Per Cent	Average Daily Slicing in Tons	Average Extraction of Sugar in Per Cent
1891–92..	178	51.52		
1892–93..	234	67.03		
1893–94..	214	62.16		
1894–95..	Not operating	——		
1895–96..	267	59.95		
1896–97..	348	64.74		
1897–98..	357	64.78		
1898–99..	294	71.33		
1899–00..	251	71.40	1193	82.49
1900–01..	Not operating	——	1044	81.92
1901–02..	Not operating	——	1418	82.67
1902–03..	318	79.20	1420	89.37
1903–04..	337	80.50	1432	83.23
1904–05..	367	78.56	1696	85.30
1905–06..	323	77.07	1498	87.86
1906–07..	306	78.68	1650	85.82
1907–08..	333	75.48	1643	90.52
1908–09..	362	68.76	1744	89.63
1909–10..	283	66.55	2142	90.38
1910–11..	364	73.40	2600	90.30
1911–12..	394	70.12	2657	90.12
1912–13..	395	73.81	2443	93.93
1913–14..	412	71.61	2406	90.82
1914–15..	400	74.42	2822	90.04
1915–16..	441	75.20	2715	92.86
1916–17..	430	72.92	2602	95.25
1917–18..	427	73.61	2327	92.82
1918–19..	468	87.61	2035	96.02
1919–20..	444	86.46	2096	97.30
1920–21..	468	86.52	2536	97.29
1921–22..	510	88.93	2780	97.13
1922–23..	496	90.15	1170	97.01
1923–24..	533	88.98	1600	97.43

Factory B, although likewise one of the older plants of the country, is one of the largest and more efficient plants. Here, however, changing agricultural and economic conditions have had an adverse influence on the supply of raw material, and during the past half dozen years an irregular or short supply of raw material has not permitted this plant to develop its maximum efficiency in all directions.

Note the slow, but appreciable, increase in slicing capacity with the years. This increase was brought about not by additions to

the size of the plant. Although weaknesses as they developed were strengthened, in Factory A the original diffusion battery of fourteen cells is still in service and a few years ago one additional cell was added. The increase in slicing capacity is due largely, however, to a better trained operating force, to the elimination of a multiplicity of interruptions, mechanical and chemical. As the process is practically continuous, an interruption at any one point stops the operations of the entire plant. In the early years of the industry in this country, it was the usual practice to close down the entire plant once each week for no less than 24 hrs. in order to go over the entire equipment. This was due in part to necessity and in part to merely a bad habit imported from abroad. It was often necessary to "boil out" the evaporator heating surfaces with acid solutions, each week, and to remove the enormous scale deposits that formed. Today, owing to the careful control and the elimination of lime salt formation, evaporators occasionally run through 80 to 100 days, without excessive fouling of the heating surfaces. Further-more, improved arrangements have been made, by which any effect of a quintuple effect evaporator, can be boiled out without seriously interrupting the operations of the remaining effects. This, and numerous other factors, account for the increased capacities over those originally obtained. There are many plants in this country that obtain proportionately, even greater increases than those shown in the table. In this direction American beet sugar operators have outdistanced anything accomplished in European practice. European sugar men usually look with astonishment at the slicing rate obtained in this country from given equipment.

Equally gratifying, is the increase in extraction, i.e.—the recovery of sugar in terms of the percentage introduced in the beets. It should be pointed out, that in the case of Factory A, the Steffens process for the recovery of sugar from molasses, was installed in 1917; up to this time this was a milk of lime, non-Steffens plant. Factory B, however, was originally equipped with the Steffens process and its extraction is wholly from that of sugar introduced in beets since no additional sugar in the form of molasses, or otherwise, was introduced. Conditions in this house are unusually favorable for a high extraction. However, it was not always so, and the improvement is due mainly to a very rigorous chemical control, with the full cooperation of the entire operating force. Just what this

TABLE III.

COMPARISON OF FUEL CONSUMPTION IN TWO PLANTS DURING A PERIOD OF 33 YEARS

Year	Factory "A" Coal		Factory "B" Oil	
	Per Cent on Beets	Per Cent on Sugar Produced	Per Cent on Beets	Per Cent on Sugar Produced
1891–92..	23.65	353.30		
1892–93..	26.90	288.30		
1893–94..	34.70	426.48		
1894–95..	Not operating	——		
1895–96..	19.40	317.72		
1896–97..	20.50	246.80		
1897–98..	21.37	242.76		
1898–99..	19.00	195.10		
1899–00..	19.00	186.75	16.64	116.3
1900–01..	Not operating	——	21.14	142.0
1901–02..	Not operating	——	18.16	133.7
1902–03..	22.56	211.90	17.54	124.4
1903–04..	22.20	181.71	15.31	108.8
1904–05..	21.50	188.33	11.94	87.3
1905–06..	22.58	332.72	12.71	81.90
1906–07..	24.99	228.76	12.67	886.00
1907–08..	22.26	180.94	12.40	77.30
1908–09..	18.44	185.78	10.48	63.00
1909–10..	21.21	235.31	9.77	60.10
1910–11..	20.28	169.13	8.48	49.80
1911–12..	18.60	141.62	8.66	50.00
1912–13..	19.00	151.66	9.78	52.80
1913–14..	17.90	157.54	9.30	53.25
1914–15..	18.18	172.92	9.16	52.14
1915–16..	19.14	154.15	9.88	57.49
1916–17..	17.58	173.09	10.29	55.98
1917–18..	18.36	220.02	11.26	59.02
1918–19..	17.21	135.92	10.17	61.10
1919–20..	15.36	140.71	10.01	54.97
1920–21..	16.92	140.26	9.39	51.45
1921–22..	15.92	119.52	8.82	49.95
1922–23..	16.55	131.26	12.67	66.84
1923–24..	15.24	135.51	10.86	56.62

difference in sugar recovery may mean, in the financial results, may readily be seen from a few figures. Factory B, during several of its operating seasons, has introduced more than 100,000,000 lb. of sugar, a difference of 1 per cent in the extraction means 1,000,000 lb. of sugar at 5 c. per lb. worth $50,000.00 for each per cent. The extraction of Factory B, during recent years has been more than 10 per cent above the results of the early years of its life, and 10 per cent means half a million dollars worth of additional sugar re-

covered per season. This shows the possibilities and rewards of a closer technical control and increasing efficiency.

Factors Affecting Fuel Consumption

Similar progress has been made in other directions as shown in Table III. The figures for Factory A are given, not because they are particularly meritorious, for they are not, (there are many plants that fall below 100 lb. of coal per 100 lb. of sugar), but rather because as a pioneer plant, its record does show the results obtained during the early days of the beet sugar industry in this country, and the progress that has been made since that time. In considering Factory A, it must be remembered that the Steffens process which increases the fuel consumption in per cent of beets, although not necessarily in per cent of sugar produced, was added in 1917. Minor fluctuations of fuel used, especially in relation to per cent of sugar produced, are due to a difference in the quality of the beets, to a difference in the quality of the fuel and to factors not within the control of the factory operators, such as an inadequate supply of beets. In the main, however, the tendency of fuel consumption has been downward, especially on the basis of sugar produced, until today, a fair average figure, the country over, is in the neighborhood of one pound of coal per pound of sugar produced.

Many factors are responsible for this decreased fuel consumption. One of the most important, is the increase in slicing capacity since there is a certain fixed fuel consumption due to power requirements and radiation losses. This aptly termed "over-head" of fuel consumption, decreases with increasing capacity. Radiation losses of course, have been reduced by better and more extensive insulation, and the power requirements and friction losses have been lowered although the actual heat or fuel requirements for these items are of lesser importance since all exhaust steam is fully utilized for heating and evaporation. Multiple utilization of vapors, not only by the fairly general use of quintuple evaporators, but also by the use of low pressure vapors for heating vapors below atmospheric pressure, where this is applicable have been in a large measure responsible for lowering fuel consumption. The increased extraction has had its influence in reducing fuel to sugar consumption. Increased boiler house efficiencies, such as the careful utilization of the hot condensates for boiler feed have added an important share in reducing

fuel consumption. A better criterion of process steam economy, would be steam consumption, rather than fuel consumption, but records of steam consumption or water evaporated in the boilers in the early years were not kept. Equally interesting data could be shown, although not always indicative of the same degree of progress, of the other materials entering into the process but a recital of such additional data would perhaps prove monotonous to all except perhaps sugar technicians.

A full measure of success has attended the efforts toward labor reduction. In the early days of the industry in this country from 6 to 8 factory labor hours were required per bag of sugar of 100 pounds. Recently one of the members of the Institute, H. W. Dahlberg, reported that the most efficient factories under his observation, had obtained figures of 29 minutes of operating labor per bag of sugar. And the ultimate limit has not yet been reached.

Now, while the quantity requirements of materials and labor have decreased, the cost of these items have not decreased in anything like the same proportion. The quantity of coal required per ton of beets has been cut into half or less, but the cost of coal per unit has doubled or more, leaving the actual cost of coal per ton of beets worked, as great or even greater. In the matter of labor, there has been an actual net reduction of costs, even though labor costs per unit of time have increased three to four hundred per cent.

The cost of the raw material, beets, has actually increased throughout the years.

The greatest single factor responsible for the decreasing market price of sugar through the years is to be found in the increased extraction, or percentage recovery of sugar in the raw material, and to this technical accounting has contributed a large share.

Discussion

President Reese: I am sure you all have found this a very interesting paper. In fact, a great part of my time has been taken up, in the last twenty years, with the economical control. I was also interested in learning that the sugar people cooperate in stating their figures and, I have no doubt, derive great benefits therefrom.

Is there any discussion of the paper?

Prof. Alfred H. White: Mr. President, let me say a word in appreciation of this paper by Mr. Zitkowski. We hear a great deal

about the value of research, but it is very rare that we get a concrete example of what a corporation has accomplished through twenty years of continuous technical control and investigation all along the line. These changes have not been made because of any one revolutionary invention. It has resulted from the close attention of many men to many points. This is a paper which I think we may cite with good effect when occasion arises.

PRESIDENT REESE: I might say we can get other papers along this line, of an historical nature, which would be extremely interesting, and I think I know where something of this kind can be gotten.

SOME FACTORS AND PRINCIPLES INVOLVED IN THE SEPARATION AND COLLECTION OF DUST, MIST AND FUME FROM GASES

By EVALD ANDERSON

Read at the Denver Meeting, July 16, 1924

Introduction

The problem of the separation and collection of dust and fume is constantly becoming more and more important. In many fields the increase in population around manufacturing establishments and the greater demand for an unpolluted atmosphere, have made it necessary to prevent the emission of dust and fume into the air where previously such contamination was of no consequence. In other fields the more modern methods involving fine grinding, flotation and greater draft through furnaces, have brought about a large increase in the dust loss and made dust collection an economic necessity. In yet other fields the partial or complete volatilization, hitherto accidental, for the separation of the values, has made the fume collection one of the main steps in the process.

It is nearly always the chemical engineer who is called upon to deal with this problem, and a discussion before a convention like this of some of the factors and principles involved, seems, therefore, appropriate.

The following plan will be followed in this discussion: First, the nature of the dust, fume and mist with which we have to deal, will be considered.

Then the main methods which are used for the separation and collection of this suspended matter will be enumerated and described.

And, finally, the factors and principles involved in the various methods will be discussed.

For the sake of convenience in this discussion, the term "suspended matter" will be used and defined as any solid or liquid particles suspended in a gas.[1] Such suspended matter is of two

[1] A good term for such a system of suspended matter is needed. It is suggested that gas-dispersoids could be used.

main classes, solid and liquid. In each class there are two types of particles; one type is made by disintegrating larger masses or bodies of the material, as by grinding and spraying. Such particles, when solid, will be termed "dust," and when liquid will be termed "spray." The other type of particle is made by condensation from the vapor phase, and the solid particles of this type will be called "fume" and the liquid particles will be called "mist." It is obvious that these terms are more or less arbitrary. Sulfuric acid mist, for example, is ordinarily called fume.

The Nature of the Suspended Matter

One of the important characteristics of suspended matter which affects its separation and collection is that of size. It is evident that the dust and spray which are produced by the disintegrating of larger masses, contain particles that are comparatively large, while the particles in mist and fume must be comparatively small. There can, however, be no sharp dividing line, based on size. Certain disintegration processes undoubtedly produce some particles as small as those obtained by condensation from the vapor phase; and on the other hand, fume and mist particles which originally might be of molecular dimensions, often grow fairly large through agglomeration.

Many measurements have been made of the diameters of different types of dust and of fume. Among the more recent ones are the following by Messrs. Drinker, Thomson and Fitchet (*Journal of Industrial Hygiene*, Vol. V, No. 5, September, 1923) showing talc dust averaging 9–10 microns; silica dust 3–5 microns; ammonium chloride fume about 1 micron, and tobacco fume particles too small to measure with their apparatus.

Herman Rohmann (*Zeitschrift fur Physik*, Vol. 17, No. 4, 1923) measured the diameter of the average particles in pigments. These varied from 2 to 5 microns.

Ordinary cement dust may be a mixture of cement material, coal-ash particles and alkali fume. A recent measurement in these laboratories of the diameters of the particles in such a sample, showed rock fragments as large as the openings in a 200-mesh screen, or 70 microns, although most were no larger than 40 microns; coal-ash spheres from 5 to 10 microns; and alkali fume particles from 1 to 5 microns. The latter also occurred in clusters or aggregates as large as 30 microns across the largest diameter.

The sizes of liquid suspended matter, such as spray and mist particles, can, obviously, not be readily determined. Ordinary zinc dust can, however, be considered as solidified spray or mist, for it is either made by spraying molten zinc and allowing the spray to cool and solidify to a dust, or by vaporizing zinc and causing the vapor to condense into a mist and then to cool and solidify into a fume.

Our determination of the diameter of the particles in the first type of dust averages about 15 microns, while in the second type the average particle is about 2 microns across. It is probable that the size of the liquid suspended matter is about the same as that of the solids. It is evident, therefore, that dust and spray particles may vary in size from 75 to 3 microns or less, and the mist and fume particles from 3 to a fraction of a micron.

The difference in size can evidently introduce large differences in the behavior of the suspended matter since a difference of 1 to 10 in the diameter would be 1 to 100 in the surface and 1 to 1000 in the volume of the particles.

Another characteristic of the suspended matter which probably largely influences its behavior is the nature of the surface. Liquid spray particles are probably spherical with smooth surfaces, but dust particles from grinding operations are necessarily very uneven. Moreover, it sometimes happens that the dust is present in gases which also carry condensable vapors, and then part of the vapor will condense as mist or fume particles on the surface of the dust particles. Thus in cement kiln dust a considerable proportion of the alkali salt occurs as small spherical fume particles which are attached to the surface of the cement dust particles proper. This fact not only prevents the clean separation of cement dust and alkali salt by settling or similar means, but also causes the behavior as regards the separation of the cement dust in a mill where there is very little alkali in the cement material, to be very different from that in the mill where considerable alkali salt occurs.

The agglomeration of fume and mist particles and the occlusion or entrainment of gases between such particles also introduce variations in the behavior of the suspended matter. With many types of collection apparatus the extent and character of the surface and the specific gravity of the particles are important variables; and it is evident that both the condensation of fume on the surface of a dust particle and the agglomeration and entrainment of gases

by fume and mist particles must largely influence their behavior in such apparatus.

Another factor which may some times affect behavior of the suspended particles is their electrical charge. This is, however, not apt to be as important as many believe. One might reason from the well known importance of the electrical charges on dispersoids in certain liquids that the dispersoids in gases should be analogous. There is, however, a vast difference between the two cases. The ordinary aqueous solutions carrying dispersoids are highly ionized, and even distilled water which is so weakly ionized as to be considered an excellent insulator, contains about one thousand billion times as many ions as are formed per second in an equal volume of air at ordinary temperature.

Gases from furnaces are naturally much more highly ionized than ordinary air so that if the dispersoids are present in the gas at the moment of ionization or before the ions disappear through recombination, a greater number of the particles might be expected to carry charges. Wells and Gerke (*Journal of American Chemical Society*, Vol. 41, 1919, page 312) state that in their oil smoke about one-third of the particles were charged, about equal numbers positively and negatively. Certain experiences in the field of electrical precipitation indicate, however, that this proportion of charged particles does not ordinarily exist for it is impossible to precipitate more than a very insignificant fraction of the dispersoids present, even from furnace gases, by the use of the electrostatic field alone.

The electrical charge of the particles, however, undoubtedly affects the rate and extent of their agglomeration. In one process for the collection of tar, the gases carrying the suspended tar particles are subjected to an alternating electrical discharge, which so increases the charges and consequent agglomeration of the dispersoids that they can be separated and collected by the ordinary inertial or gravitational means.

Methods of Separation and Collection

The various methods used for the separation and collection of suspended matter from gases may be divided into five main classes:

1. *Gravitational Methods*

These are used in settling chambers, whether the ordinary large dust chamber, or the more modern scientifically designed Howard dust catcher.

2. *Inertial Methods*

The inertia of the particles is the basis for the operation, both in the ordinary baffle chambers and the more modern nozzle type apparatus, as well as in the centrifugal type of dust catchers like cyclones and dust collecting fans.

3. *Filtration Methods*

The familiar baghouse is an example of this method, but many other filtering means are used for the collection of dust and fume. The inertia method is combined with the filtering method in that class of so-called filters where the filtering medium is comparatively coarse but covered with a sticky material, so that the suspended matter in the gases collides with this material and adheres to it.

4. *Spraying Method*

This method is used in the ordinary spray tower where liquid particles are made to pass through the gas so as to carry the suspended matter with them. A combination of the inertial and spraying methods is used in the centrifugal washers, and certain other types of scrubbers.

5. *Electrical Methods*

The only process based entirely on electrical methods is that of the so-called Electrical Precipitation. There are also combinations of electrical and inertial methods where electrical discharge is used to agglomerate the dispersoids and where the agglomerated particles are later collected by inertial means.

Analysis of the Principles and Factors Involved in the Different Separation Methods

Gravitational Methods

The fundamental factor involved in the separation of suspended matter by gravitational methods is the velocity imparted to the particles by the force of gravity, or, in other words, the rate of settling. Since the force of gravity is constant, this rate depends on the resistance of the gases to the motion of the particle. The resistance varies principally with the size and velocity of the particle and viscosity of the gas, and the quantitative relation of these variables is expressed in Stokes law. From this law the following

simplified expression can be derived for the final velocity acquired by a small particle falling in a gas:

$$v = \frac{gd^2\rho}{k\eta}, \tag{1}$$

where v is the velocity of the particle with respect to the gas,
d is the diameter of the particle,
ρ is the density of the particle,
g is the acceleration due to gravity,
η is the viscosity of the gas,
k is a constant.

In calculating the rate of settling, this expression is valid only where the velocity of the gas itself is zero. One might, however, expect it to hold at least approximately, in the case of horizontally moving gases as long as the velocity is less than the critical value so that the motion is not turbulent.

The critical velocity is itself a function of the viscosity of the medium and for gases it is in most cases less than 1 ft. per second.

Stokes law also presupposes that the particles are spherical, which undoubtedly is never the case with ordinary dust.

Nevertheless, it is instructive to calculate what would be the velocity or rate of settling in the ideal case, in order that it may be compared with the rates actually found in practice.

The figures in the following table have been calculated from the expression just given. The viscosity of the gas has been taken as that of air or 1.8×10^{-4} c.g.s. units, and the density of the particles as 3.0 gm. per c.c.

The diameter of the particles is given in microns or thousandths of a millimeter. The first column gives the nearest screen mesh in two cases.

Rate of Fall of Spherical Particles in Still Air

Screen mesh	Diameter of particles, microns	Rate of fall, ft. per sec.
155	100	3
200	74	1.6
	10	.03
	1	.0003

It is evident from the above table that the rate of fall of the particles decreases very rapidly with their size so that unagglomer-

ated fume or mist which probably often largely consist of particles 1 micron in diameter, would scarcely settle at all in the ordinary settling chamber.

It is very difficult to obtain any actual data for ordinary dust under conditions which are comparable with those assumed above. This is largely so because of the uncertainty of the sizes of the particles, and the number of each size.

The following data have been obtained from tests with metallurgical and cement dust, and while no great accuracy can be claimed, they nevertheless indicate the order of magnitude of the settling rates that can be expected. The tests were made with gas velocities between 2 and 4 feet per second so that the motion was turbulent. The greater part of the data refers to metallurgical dust and to that part of the dust which all passed a 200-mesh screen, but some figures have also been obtained on that which passed 150- but not 200-mesh.

The density of this dust was about 3.0 gm. per c.c., and the viscosity of the gases was near that of air at ordinary temperatures. The average rate of settling of the dust between 150- and 200-mesh was about 0.9 ft. per sec.

This velocity refers to the finest of the particles, or in this case to the 200-mesh material. It can, therefore, be compared with the theoretical rate of fall for particles of this size.

It is thus seen that, while in still air the rate of fall of a 200-mesh particle with a density of 3.0 is 1.6 ft. per sec., the rate of fall of such a particle in gas which is moving with a "turbulent" velocity is only 0.9 ft. per sec., or 56 per cent of the theoretical value.

In the tests on that part of the material which all passed 200-mesh and which, therefore, consisted of particles 200-mesh and finer, no figures could be obtained for the rates of fall of any given size particle. The data were, therefore, calculated to show the rate of fall of the fastest settling particle which remained after varying percentages of the initial dust had been settled out.

Two series of tests were made. In one a straight open dust chamber was used, and in the other wires were hung throughout the entire length of the chamber. These wires naturally tended to make the motion less turbulent and more nearly the "straight line" type.

It is evident that, when gases carrying dust which consists of particles of varying sizes, enter a settling chamber and move

horizontally, the heaviest particles will settle out first. The largest particle remaining in the gas after, say, 50 per cent of the initial amount has settled out, will be larger and settle at a faster rate than a similar particle after 75 per cent had settled.

It was found that if the settling rates of these largest particles were plotted against the percentage of dust settled, the graphs were straight lines with approximately the following equations:

$$\left.\begin{array}{ll} (2) & v = -.012P + 0.98 \\ (3) & v = -.012P + 1.06 \end{array}\right\} P < 80 \text{ per cent}$$

In these equations v represents the settling rate, in feet per second, of the fastest settling particles which remain suspended after P per cent of the initial dust had settled out. Equation 2 represents conditions in the straight settling chamber, while Equation 3 represents conditions in the chamber hung with wires. The data included percentages of settling of from 45 per cent to 80 per cent, and although the graphs were straight lines up to these percentages, it is evident that the equations can not hold true for settling percentages much over 80 per cent, since the line should become asymptotic with the zero velocity line at 100 per cent.

It is thus seen from Equation 2 that when 50 per cent of the dust had settled out, the rate of the fastest settling particles was

$$v = -.012 \times 50 + 0.98 = 0.38 \text{ ft. per sec.}$$

For the same settling efficiency with the wire hung chamber the velocity would be 0.46 ft. per sec.

Since the dust in this test was all less than 200-mesh, the largest particles before any settling took place would be just this size. The settling rate of these particles can be obtained from Equation 2 by making P equal to zero. The settling rate, v, thus becomes 0.98 ft. per sec., which is in fair agreement with that previously obtained from the tests on dust with particles just larger than 200-mesh, of 0.90 ft. per sec.

In similar, but less elaborate tests with cement dust, the velocity corresponding to 52 per cent settling was found to be 0.30 ft. per sec. This is in agreement with Equation 1, if allowance is made for the density of the material, being 2.6 instead of 3.0.

This settling velocity of the fastest particles leaving a settling chamber is also the settling velocity of the slowest particle that would

reach the bottom of the chamber if starting from its top. Consequently if a chamber is designed with such a height and length for a given gas velocity that a particle at the top with this settling rate would just be caught, the total collection in the chamber would be as indicated by P in the above equations. If one allows for the density of the dust, ρ, and neglects the viscosity of the gas, the Equation 2 can be put in the following approximate and more general form:

$$v = \frac{\rho}{3}(1.0 - .012P). \tag{4}$$

The discussion of these factors in dust settling and of the rather fragmentary experimental results has been longer than perhaps the subject would seem to warrant. Judging by the type of settling chambers built, however, there does seem to be often an entire lack of understanding of the fundamental ideas involved. For example, there is evidently little advantage in obtaining large cross-sectional area by making a chamber very high, since the additional settling distance just counteracts the decreased velocity. Yet very high chambers are the rule, rather than the exception.

In designing a settling chamber it would seem that the first step should be to determine the average settling rate of the suspended matter to be collected. This can be done by construction of a small experimental unit, and determining the actual settling rates by such means. If this is not convenient, a sample of the suspended matter can be filtered out and the sizes of the particles estimated. The settling rates can then be calculated with sufficient accuracy by using Stokes law and a correction factor of about 0.5 for the effect of the gas velocity. If either one of these methods is not convenient, at least the approximate settling rates can be calculated by the use of the above Equation 4. After the settling rates have been determined, a chamber can be designed with appropriate cross-section, height and length, so as to insure that the desired proportion of dust will settle in the time that the gases remain in the chamber.

It is obvious that the chamber should be made as low as economically and practically possible, and the design should be such as to insure an even gas flow throughout the length of the chamber. This latter feature is more important than ordinarily realized, and it is probably always advisable to install a few curtains of wires or chains across the chamber at different points so as to break up

eddy currents and make the gas flow more nearly like the stream-line type.

Inertial Methods

In these methods also one of the fundamental factors involved is the resistance of the gas to the motion of the particles, and here also Stokes law gives the quantitative relation between the force applied and the rate of motion of the particles. The other factor is the force causing the particles to move out of the gas stream which in this case is the centrifugal force instead of gravity. This force depends on the velocity of the particle in the direction of the gas stream, on its mass, and on the curvature of the path of the gas.

The relation between the velocity, v, with which the particle moves out of the gas stream, and which might be called its separation velocity, and the other variables is as follows:

$$v = \frac{d^2 \rho \gamma \omega^2}{k\eta}, \tag{5}$$

where ω is the angular velocity of the gas and suspended matter,
γ is the radius curvature of the path described by the gas,
k is a constant,
and the other symbols have the same significance as in Equation 1.

In the ordinary inertial method, however, it is not the separation velocity of the particle which is important, but rather the radial distance D that the particle will move out of the gas-stream, while the gas is in the apparatus.

If we assume that the gas moves in a circular path with a uniform velocity V, and that while in the apparatus it will move through the angular distance S, then the following equation will express the relation between the gas velocity V, the diameter of the particle d, the radial distance D, the angular distance S, and the variables depending on the nature of the suspended matter and the gas:

$$V = \frac{kD\eta}{S\rho d^2}. \tag{6}$$

In order to visualize the effect of the size of the particle on its chances of being precipitated by the use of inertial methods, the following case has been taken. An apparatus has been assumed, similar to a cyclone, but in which the entire path of the gas is circular and in a horizontal plane. The other conditions that have

been assumed are that the gas moves about two-thirds the distance around the circle, or through an angular distance of 4 radians, before escaping from the apparatus, and that the dust particles must move a radial distance of 3 ft. in order to be precipitated.

The viscosity of the gas has again been taken as 1.8×10^{-4} c.g.s. units and the density of the particle as 3.0 gm. per c.c. The table below gives the resulting relation between V and d:

Diameter of particle, d-microns	Gas Velocity, V-ft. per sec.
100	8
74	15
10	800
1	80,000

It is evident from these figures that it would be impracticable to attempt to collect a large proportion of particles much smaller than 74 microns, or 200-mesh, in such an apparatus, on account of the high gas velocities then necessary.

In another modern English apparatus, the so-called Calder-Fox Scrubber, used for removing mist from gases, the distance D that the particle must move in order to be out of the gas-stream is on the order of 1/10 of an inch, and the angular distance of the gas, S, is 90° or about 1.5 radians. With sulfuric acid mist particles with an assumed density of 1.8, the following gas velocities would be required for different sizes of particles:

Diameter of particle, d-microns	Gas Velocity, V-ft. per sec.
3	90
2	200
1	800

The actual gas velocity in the active parts of this apparatus is usually about 100 ft. per sec., so that it is possible to completely remove fume particles between 2 and 3 microns in size, in a single unit of the apparatus.

It is evident that in these inertial apparatuses it is necessary to not only force the particles out of the gas-stream but also to insure that they are not again picked up. If this were not so, it is seen from Equation 6 that an apparatus like a cyclone should become more efficient the greater the gas velocity. There is obviously a maximum velocity for each apparatus above which the precipitated dust would again be entrained by the gas.

It is interesting to note from Equation 6 that if the cross-section of the gas passage be doubled in such a way as to double the distance D, it is also necessary to double the velocity V in order to maintain the same precipitation efficiency. In other words, if the diameter of a cyclone is increased by two, the gas volume should be increased by four. This fact is probably not always borne in mind when designing larger apparatus from small size experiments.

Equations 1 and 6 can be used for developing expressions on the relative effect of the centrifugal force and that of gravity in baffled settling chambers. Thus from Equation 1 it can be shown that

$$D = k_2 \frac{gL}{V}, \tag{7}$$

where L is the length of the settling chamber,

V the gas velocity,

D the distance the particle moves out of the gas stream,

K_2 is a constant equal to $\frac{\rho d^2}{k\eta}$.

From Equation 6 it follows that

$$D = k_2 VS, \tag{8}$$

where the constant is the same as in 7 and D, V and S the same as in Equation 6.

If, then, we take a settling chamber 10 ft. long with a gas velocity of 3 ft. per sec., and take g equal to 32 ft. per sec. per sec., it follows from Equation 7 that

$$D = 109k_2.$$

Similarly, if we take a baffled chamber such that the gas is made to pass in one complete half circle, so that $S = 3 +$ radians, and of such length that with a gas velocity of 3 ft. per sec., the gas will pass through it in the same time as in the above settling chamber, then from Equation 8,

$$D = 9k_2.$$

Consequently settling is far more effective than centrifugal action at these low velocities. It is, therefore, likely that the baffles which produce tortuous motion in most settling chambers

with such low gas velocities, are a detriment to their effectiveness, rather than otherwise.

If, in the above example, the gas velocity had been taken as 10 ft. per sec., the two cases would have been as follows:

$$D = 32k_2 \text{ (gravitational)},$$
$$D = 30k_2 \text{ (inertial)}.$$

And with a 20 ft. gas velocity

$$D = 16k_2 \text{ (gravitational)},$$
$$D = 60k_2 \text{ (inertial)}.$$

Consequently with gas velocities of 10 ft. per sec., or over, the inertial effect becomes important. At such velocities baffle chambers might be expected to be effective, provided they are properly designed.

Any apparatus of this type must necessarily provide for a sufficient gas velocity and curvature of gas flow as to cause the separation from the gas stream of the desired proportion of suspended matter. It must also provide for the collection of the material, either by settling in suitable quiescent zones, or by agglomeration and adhesion at the walls of the apparatus. In any case it is likely that better results can be obtained when designing such apparatus if the fundamental principles are understood and applied in place of, or in connection with, the customary cut and try methods.

Filtration Methods—Spraying Methods

There is little to be said on the principles involved in these methods. It is obvious that in order to remove suspended matter from gases by filtration, it is only necessary to pass the gas through a filtering medium with sufficiently small interstices that the gas can pass through but not the suspended particles.

The practical considerations involved are here the all important ones. For example, the filtering medium must obviously be of such nature that it is not attacked either by the gas or by the suspended matter. Then there must be sufficient power available to force the gases through the medium even when an accumulation thereon of the separated material tends to reduce its permeability.

Provision must also be made to periodically or continuously remove the separated material from the filtering medium so as to

prevent too high a draft loss. Much ingenuity has been displayed by the different inventors and manufacturers to facilitate such a removal.

Lastly, the temperature and humidity of the gases must be maintained within fairly narrow limits, so that the filtering medium is not destroyed by heat, and so that the material does not become wet and clog the medium.

Mist is sometimes filtered, but in such a case the filter usually acts simply as an agglomerator and serves to cause the mist particles to coalesce into drops which then pass through the filter and are collected by gravitational or inertial methods.

In a spray tower, the size of the drops, i.e., the degree of dispersion of the filtering medium should be regulated in accordance with the size of the suspended matter. It is evident that the interstices between the drops in any plane will be larger, the larger the drops, for any given weight of liquid, so that, while comparatively coarse spray might be effective in removing dust, a fine spray might be necessary for the removal of fume.

In this method the inertia of the suspended matter and of the spray particles plays a part. Thus a curtain or column of liquid spray particles is similar in its action to a filter where the medium is covered with some "sticky" material. It is, therefore, desirable that the velocity of the drops, relative to that of the gas be as great as practicable, so that the inertia of the suspended matter will prevent its being carried out of the path of the drops with the gas.

In the spray method it is not only necessary to collect the suspended matter from the gas on the liquid filtering medium, or spray, but also to remove the latter from the gas. In doing this, either inertial or gravitational methods are effective as long as the sizes of the drops are large enough. While there is no fundamental relation between the gas velocity and the separation of the suspended matter, in either method, practical considerations set an upper limit. In the ordinary filter too high velocity causes excessive power losses due to the increased resistance to the gas flow, and in the spray method a high gas velocity tends to carry away the liquid.

The problem of removal of the separated suspended matter from the filtering medium is comparatively simple in the ordinary filter. In the spray tower the suspended matter may either be dissolved in the medium, or may be carried in suspension. In

either case the recovery of the suspended matter involves considerable effort.

Electrical Methods

The two methods to be discussed under this heading are Electrical Agglomeration and Electrical Precipitation.

In the Electrical Agglomeration method, the gas carrying the suspended matter is passed between two electrodes from one of which an alternating electrical discharge takes place. In this manner ions first of one sign and then of the other are caused to pass through the gas. The suspended particles may then be ionized through contact with either positive and negative ions so that positive and negatively charged particles result. Some of these charged particles undoubtedly are forced to the electrodes, but owing to the alternations of the field, the proportion so precipitated is small. The remainder tend to combine with each other so that the smaller mist and fume particles form into larger aggregates.

These larger aggregates are then more easily separated from the gas by gravitational or inertial methods.

The Cottrell Electrical Precipitation method for the separation of suspended matter from gases is unique in many respects. It is not limited by the size of the particles as are the gravitational and inertial methods. Nor is it limited by the resistance to the motion of the gas as is the ordinary filter or certain scrubbers, for though it may be considered as a filter or scrubber with streams of ions as the medium, its resistance to gas flow is negligible. Moreover, the ions which act like fine spray particles in removing the suspended matter from the gas cannot be carried out of their regular paths like the light spray particles, for they are kept moving by forces independent of the motion of the gas, which are much greater than the inertial and gravitational forces which act on the spray particles.

The apparatus used in this method, and its operation has been described so often in the literature as to undoubtedly have become familiar to all Chemical Engineers. The principles involved have also been discussed by many writers, and since this phase of the question is of particular interest here, a list of some of these articles is given below.[2]

[2] List of Articles on Electrical Precipitation

F. G. Cottrell, *J. Ind. Eng. Chemistry*, Vol. III, August, 1911.

In the Electrical Precipitation method, as in the gravitational and inertial methods, the motion of the particles out of the gas stream is the fundamental phenomenon. In the above two methods this motion depends on the gravitational and inertial forces, and on the mass of the particles; in this method it depends on the electrical force and on the electrical charge of the particles. The function of the apparatus, commonly called the precipitator, used in this method, is, therefore, two-fold; it must both provide the electrical force, or field, and also charge or ionize the particles.

It is likely that of these two functions the ionization is the more important. Thus, while in the gravitational method the proportion of the suspended particles that is separated depends on the settling velocity, in this method it probably depends chiefly on the proportion of particles that become ionized; for it is likely that the separation velocity of the particles that do become charged is so great that they will always move out of the gas stream in much less time than the gas remains in the apparatus.

The gaseous ions which are formed at the discharge electrode move in nearly straight lines or streams, through the gas to the collecting electrode. Uncharged gas molecules are also carried along in these streams, so that these are in fact currents of gas, sometimes referred to as electrical convection currents. A particle, in order to become ionized, must get in the path of these ion streams. It then moves to the collecting electrode under the action of the electric force or field.

Some writers have attempted to calculate the resultant velocity of these charged particles with the aid of Stokes law as the settling velocity of a particle is calculated. It is evident that such a calculation only gives the velocity with respect to the gas, and since, in this case, there is an appreciable gas velocity in the same direction as the particles move, such calculations must be inapplicable.

The velocity of a single gaseous ion in a precipitator may be 100 ft. per sec. or more. The separating velocity of the suspended particle in a precipitator would ordinarily need to be less than 1 ft. per sec. in order to be precipitated so that it is evident that it must

W. W. Strong, *J. Franklin Inst.*, Vol. CLXXIV, September, 1912. *Met. and Chem. Eng.*, June 1, 1917.

F. Mickel, *Revue Generale des Sciences*, August 30, 1918, p. 295.

J. Saget, *Revue Generale d'Electrisitet*, April 13, 1918.

Herbert Thein, *Zeitschrift fur Technishes Physic*, July, 1921.

be the proportion of particles ionized, and not their resultant velocity which determines the rate of precipitation.

The number of singly charged ions passing through the ordinary precipitator is tremendous compared with the number of fume particles. Assuming a fume concentration of 2 grams per cu. ft., which is much over normal, and also assuming that this fume is all present as single particles with a diameter of 1 micron and density of 2.5, there would still be 10,000 ions present for every fume particle.

The ionization of the suspended particles, therefore, undoubtedly depends on the chance of the particle getting in the path of the ions, and this chance is necessarily greater, the larger the number of particles exposed to a gas ion stream.

If we then assume that the time rate at which the particles in a given space become ionized by the stream of ions, and thus precipitated, is proportional to the concentration of the particles in that space, then it can be shown that if gases carrying suspended particles remain in a precipitator for a time t, and if P is the proportion or fraction of the initial amount of suspended matter which is ionized and precipitated in this time, the following relation will hold:

$$1 - P = K^t. \tag{9}$$

The constant K in this equation has been called the precipitation constant.

The following data taken from tests on the precipitation of mist particles indicate how the results obtained agree with Equation 9. In these tests the electrical force and the character of the fume were constant and the time t was the only variable. In this table P has been expressed as per cent, instead of as a decimal fraction.

DATE FOR EQUATION $1 - P = K^t$. FROM PRECIPITATION TESTS

P, %	t, seconds	$K \times 10^3$, calculated
73.7	0.46	55
80.0	0.56	56
86.8	0.69	54
93.4	0.93	54
95.2	1.05	55
98.1	1.40	59

It is evident from this table that the values of K are essentially constant, so that Equation 9 is in good agreement with the facts.

The constant in this equation represents the percentage loss in a precipitator when the time t is equal to 1, i.e., when the gas velocity is such that it takes unit time for the gas to pass through the active part of the precipitator. This quantity is evidently not ordinarily constant. It varies with the electric field strength, the type of precipitator, the nature and size of the suspended matter, etc. Thus it is smaller for stronger electric fields and for suspended particles of greater size, which is to be expected. With stronger electric fields the force is not only increased but also the number of ions, and the larger the size of the particle the better should be its chances of becoming ionized. (This latter effect has been made use of by Herman Rohmann as a basis for the determination of the size of the particle. Loc. cit.)

No satisfactory quantitative relationships between the precipitation constant and these variables have, however, so far been obtained. The present art of Electrical Precipitation consists chiefly in accumulating data on these variables and in intelligently applying these data with the aid of the general precipitation equation.

HEAT TRANSFER IN STEAM-JACKETED EVAPORATORS

Determining Overall Transmission and Film Coefficients as Well as Operating Efficiencies on Plant Equipment over a Wide Range of Industrial Conditions

By H. L. OLIN, M. H. DOWELL and C. M. TOYNBEE

Read at the Denver Meeting, July 17, 1924

The importance of heat transfer in its relation to the design and operation of chemical apparatus and machinery is so great as to furnish ample apology for the numerous papers on the subject appearing in the current technical literature. Indeed in all the unit processes of chemical engineering, with the possible exception of crushing and grinding, heat transfer is either the primary objective or a more or less direct factor limiting the results obtained.

Among the most important contributions to the subject of heat exchange by conduction are the papers recently published by McAdams and Frost.[1] In the case of flow between fluids separated by a boundary wall these authors express the familiar Newton's equation in the form

$$\frac{Q}{\theta} = \frac{\Delta t}{\dfrac{1}{h_1 A_1} + \dfrac{L}{k_2 A_2} + \dfrac{1}{h_3 A_3}} = \frac{\Delta t}{R} = H A_{av} \Delta t, \tag{1}$$

where Δt is the overall temperature gradient, H the overall coefficient of heat conductivity and h_1, k_2 and h_3 the specific conductivities of the first fluid film, the boundary wall and the second film respectively. They deprecate the fact that most transmission data are expressed as overall coefficients and stress the importance of developing and tabulating general equations for the film coefficients for the guidance of the designer who by substituting these values in equation 1 may thereby calculate the overall coefficient and the areas of heating surfaces necessary for a given capacity under given

[1] *Ind. Eng. Chem.*, 14, 13, 1101 (1922).

conditions. On the basis of their own experimental results together with the rather meager data on the direct measurement of film coefficients to be found in the literature they propose as the formula for liquid film conductivity in the case of heat transfer from condensing steam to liquid (not boiling), under forced convection through pipes,

$$h_L = 23.6\frac{K}{D}\left(\frac{Du\rho}{z}\right)0.796, \tag{2}$$

where K is the specific conductivity of the liquid, u its velocity, p its density, z its specific viscosity and D the inside diameter of the pipe in inches. The mean straight line curve from which the preceding formula was deduced—the logarithmic graph of $(h_L D)/K$ against $Du\rho/z$—conforms closely to the points as plotted in spite of the diversity of the experimental conditions under which the various data were obtained. The conductivities of the common metals are of course available and the coefficient k_2 for the boundary wall may be easily calculated. With unit areas, the overall coefficient is now

$$H = \frac{1}{\frac{1}{h_1} + \frac{L}{k_2} + \frac{1}{h_3}}. \tag{3}$$

Without question this method of attacking the problem is thoroughly sound in principle; but whether it can replace entirely direct measurement of H is doubtful for the experimental difficulties of evaluating some of the factors involved in a film coefficient formula for cases other than that just considered may be very great, as, for instance, determining the velocity of natural convection through the tubes of evaporators. Moreover, the task of constructing a "synthetic" H is complicated by the cleanliness factor for it is obviously not easy to standardize a film that may consist of oxide, sulphide, mineral scale or oil of varying thickness, density or composition. The importance of this factor has lately been emphasized by Pridgeon and Badger.[2]

Lucke[3] is emphatic in advocating direct measurement. " . . . The practical everyday problem of deciding on how much surface to allow on a given heat flow or how much heat can flow

[2] Ibid., 16, 468 (1924).

[3] "Engineering Thermodynamics," p. 533.

past a given surface is not one that can be solved by the laws of conduction even if data on all substances were available, and probably never will be, because it requires an hypothesis fixing the thickness of the fluid film, the joint resistance, the kind and thickness of fouling or layer of dirt. Problems of this character are to be solved in another way by means of coefficients of transmission found by experiment and applied to the same kind of apparatus as that on which the experiment was made and covering all resistances together although each cannot be separated from the rest."

As in most cases of difference of opinion the truth probably lies somewhere between the two extremes.

Steam Jacket Heating

Investigations of one of the many phases of heat transfer, viz., flow in steam-jacketed evaporators, have been carried on at the University of Iowa since 1921 and the material presented in this and subsequent papers is selected from theses presented by candidates for advanced degrees in chemical engineering. Selection of this type of apparatus for study was suggested by the meagerness of published data, for while vacuum evaporation involving heat transmission through tubes has been well covered by such authorities as Hausbrand, Kerr and Badger, little attention evidently has been given to the secondary but, nevertheless, important subject of steam jacket heating. Few data of any kind that can be used in design are available, much less complete information covering pans of various kinds of metal, wall thickness, shape and condition of surface.

In scope, the work already done and immediately projected comprises studies of open evaporating pans of (1) cast iron, (2) cast iron with enamel lining, (3) cast iron with lead lining, (4) copper, and (5) aluminum. Besides these, tests are being made on a steam-jacketed copper vacuum pan and on a copper still operating at barometric pressure. The data desired are, first, overall transmission coefficients over as wide as possible a variety of conditions met with in industrial operation together with such figures for film coefficients as may be evaluated, and, second, operating efficiencies under the same specified conditions.

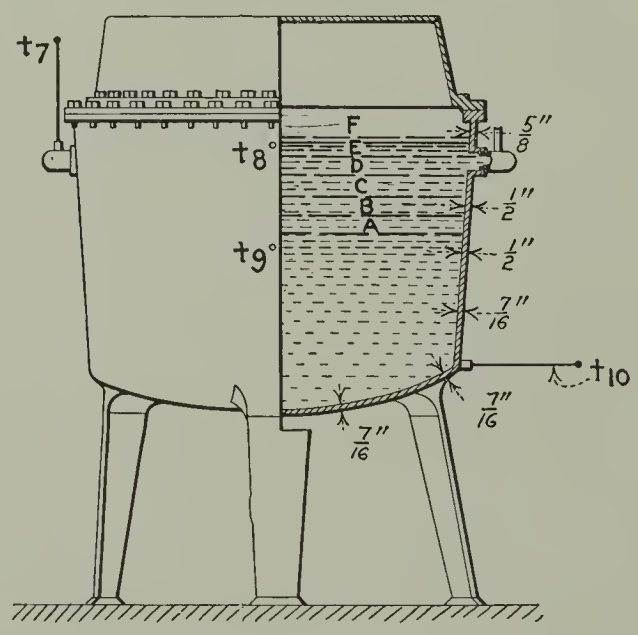
Among the variables taken into account are (1) temperature gradient, (2) hydrostatic head, (3) density of liquid, (4) viscosity of liquid, (5) velocity of convection currents as well as those pro-

duced by means of agitators, (6) radiation and (7) character of metal used in construction. The apparatus employed was in every case of experimental plant size and results are presented, therefore, with confidence so far as their application to plant conditions is concerned. Indeed, it has been our purpose so to reproduce normal plant operating conditions as to make the overall figures obtained generally significant over a wide range and thus to minimize the necessity for evaluating the more elusive film coefficients.

Methods and Apparatus

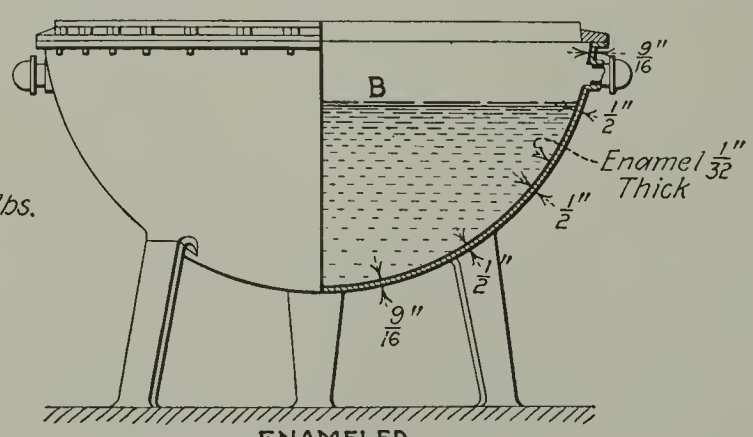
The first evaporator to be studied was a 47-gal. cast-iron kettle with 7-in. curb manufactured by the J. L. Mott Iron Works and

Level	Area (Sq. Ft.)	Head (Ft.)	Wt. of Water (Lb.)
A	9.01	1.05	200
B	9.71	1.16	225
C	10.47	1.27	250
D	11.20	1.38	275
E	11.95	1.49	300
F	12.62	1.50	325



CAST IRON KETTLE 11-X

Level B
Area 11.41 sq. ft.
Head 1.16 ft.
Wt of Water 325 lbs.



ENAMELED
CAST IRON KETTLE 111-X

Fig. 1

listed in their catalog as Plate 11-X. For the later runs this was heavily insulated with Sil-O-Cel applied in three coats. Dimensions including thickness of metal wall are given in Fig. 1. Supplementary apparatus used in obtaining heat efficiencies as well as transmission data included a Schaeffer and Budenberg separating calorimeter for measuring the quality of the steam, a highly accurate test gauge reading to 60 lb. made by the same company, a Worthington Type F duplex direct acting water meter, calibrated mercury thermometers and tanks, condensers, steam traps, barometer and platform scales. The whole set-up is shown in detailed diagram in Fig. 2. Distilled water produced in ample amount by means of

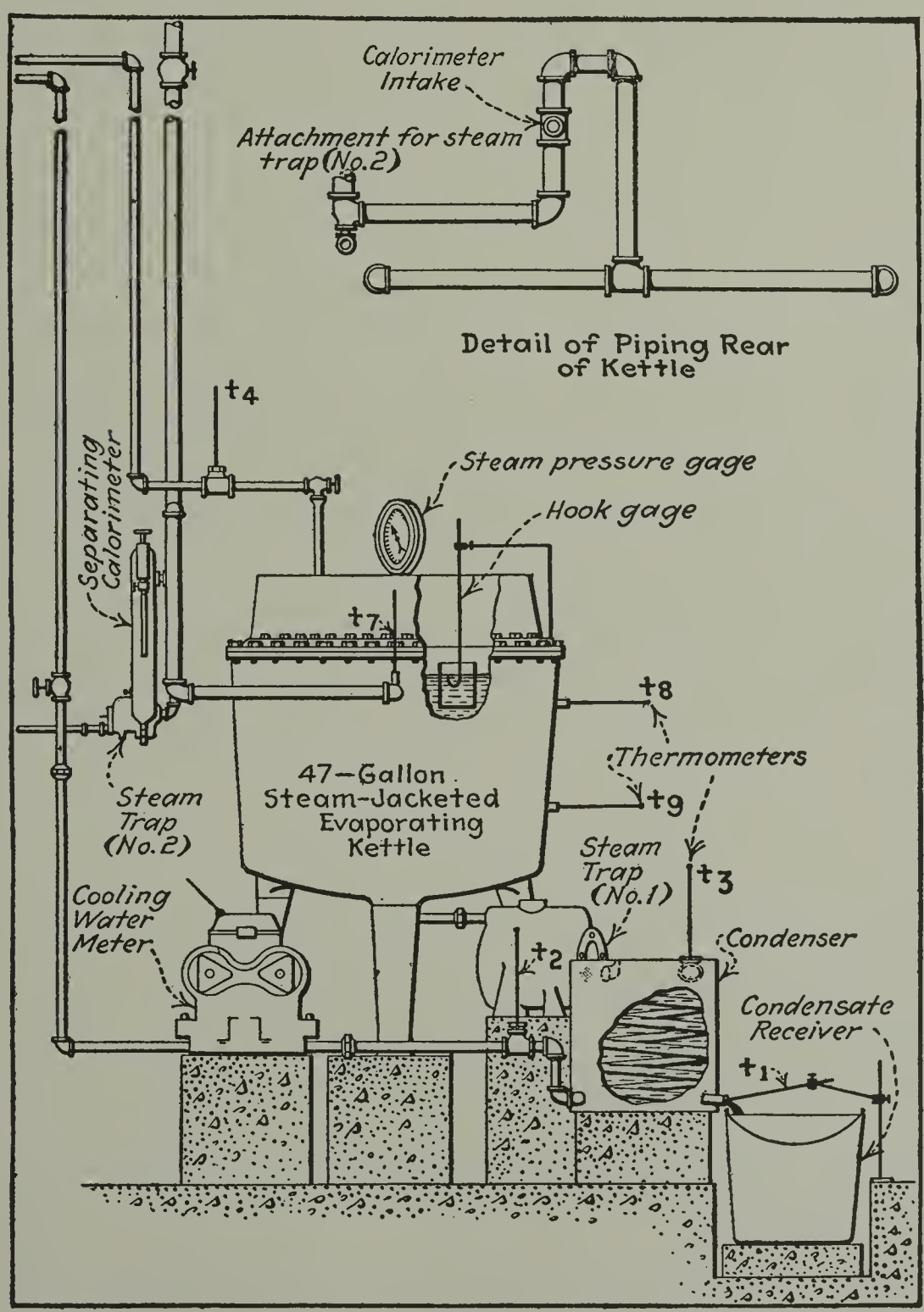


FIG. 2

a double-effect evaporator which is a part of the laboratory equipment was used throughout the work. This was supplied to the kettle from an elevated tank mounted on platform scales, and maintained at constant level with the aid of a hook gage. A copper worm condenser cooled with accurately metered water was placed in series with the steam trap for the measurement of heat leaving in the condensate. Temperature gradients used in determining the coefficient were calculated as the difference between temperature corresponding to the indicated pressure of the steam and the boiling point of the evaporating water corresponding to the barometric pressure. From the heat balance made on each run the amount of heat transmitted, as well as that lost by radiation and discharged in the condensate, were determined and from them the coefficient and the transmission and overall efficients were calculated

Heat Losses from Bare Kettles

In order to determine the loss of heat from the unlagged surface of the kettle a series of runs was made before the Sil-O-Cel coating mentioned above was applied. A tight-fitting wooden diaphragm was inserted at the junction of the curb and the steam jacket and covered with layers of paper and dry Sil-O-Cel to make it a non-con-

TABLE I

Radiation Losses from Bare Kettle Surfaces

Series 2-A

Run No.	Absolute Steam Pressure	Steam Quality	Heat Transmitted B.t.u.	Temp. Grad. Deg. F.	*U* Steam to Air	Velocity of Air, Ft. Per Min.
0	37.6	99.1	14,240	181.7	4.8	0
1	40.1	99.2	12,992	182.8	4.4	0
1*a*	40.0	98.7	14,500	185.1	4.8	0
3	50.4	99.2	14,590	196.8	4.6	0
3*a*	49.7	99.2	16,170	191.9	5.2	0
5	60.0	98.9	18,580	211.6	5.4	0
5*a*	60.0	99.4	17,940	208.1	5.3	0
7	69.8	99.6	18,980	217.8	5.4	0
7*a*	69.5	99.5	17,920	214.7	5.2	0
Series 2-B						
3	50.2	99.6	20,190	198.4	6.3	254.0
3*a*	50.6	99.4	20,930	202.0	6.4	252.0
5	61.1	98.8	21,580	211.1	6.3	220.0
5*a*	60.5	99.2	21,640	208.6	6.4	239.0

ductor of heat. A dead-air space was thus provided within the kettle and radiation was necessarily confined to the kettle walls. The first series was run with static air conditions; in the second a draft induced by a 16-in. electric fan placed at a distance of 14 ft. was directed against the apparatus, the velocity at the surface being measured by means of a delicate anemometer. Results obtained are shown in Table I.

The nature of this special case made necessary the calculation of heat radiated as the difference between that supplied and that removed through the condenser. In all other cases transmission was measured by the amount of water evaporated.

Effect of Temperature Gradient and of Hydrostatic Head

The apparatus with the insulating jacket as described above was used in 6 series of tests to determine what influence the height of water level and the temperature gradient exert on transmission. Fig. 1 shows the variation in level and of heating surface through the range of heads from 1.05 ft. to 1.59 ft. In each case the time of run was 30 min. measured with a stop watch, and readings were taken at 3-min. intervals.

TABLE II

Effect of Temperature Gradient and Hydrostatic Head

Series III–A

Head = 1.05 fr.

Run No.	Abs. Steam Press. Lb. per. Sq. In.	Steam Quality Per Cent	Heat Trans-mitted B.t.u.	Overall Eff. Per Cent	Trans-miss. Eff. Per Cent	Temp. Grad. Deg. F.	*U* Steam to Water	Water Evapo-rated Lb.
Run No.	Abs. Steam Press. Lb. per Sq. In.	Steam Quality Per Cent	Heat Trans-mitted B.t.u.	Overall Eff. Per Cent	Trans-miss. Eff. Per Cent	Temp. Grad. Deg. F.	*U* Steam to Water	Water Evapo-rated Lb.
1	37.5	97.7	62,320	75.3	91.9	50.6	273	56.0
1*a*	38.9	96.9	65,340	62.0	94.4	54.1	268	59.0
2	43.9	96.9	73,090	79.1	94.9	60.4	269	66.0
2*a*	47.2	98.0	82,340	72.0	89.4	65.4	280	74.0
3	49.7	97.3	93,730	76.4	94.8	69.6	299	81.5
3*a*	49.8	97.9	82,670	69.3	88.1	70.4	261	78.0
4	53.1	98.5	92,570	75.6	87.6	73.4	280	80.5
5	58.8	97.2	101,520	69.4	86.6	79.4	284	100.0

Series III–B
Head = 1.16 fr.

1	39.4	97.0	—	—	—	55.4	—	70.0
2	44.7	98.1	77,680	70.8	86.8	63.1	256	75.0
3	49.2	97.6	91,080	70.4	87.7	69.0	271	88.0
3*a*	49.9	97.4	94,380	73.1	92.0	70.6	275	89.0
4	54.3	98.1	94,420	67.6	84.5	75.3	258	93.0
5	59.0	97.8	102,670	66.7	84.8	80.6	265	101.0
5*a*	59.1	97.7	108,050	66.7	84.8	80.1	278	106.5

Series III–C
Head = 1.27 fr.

1	38.2	97.3	61,360	70.6	88.3	53.3	229	62.0
2	44.1	97.6	78,930	70.0	87.3	62.0	248	77.5
3	49.7	97.1	95,240	69.4	87.9	69.4	261	93.5
3*a*	49.7	97.3	96,160	70.8	89.1	70.1	262	90.5
4	54.0	97.7	100,840	67.5	85.3	74.6	258	98.0

Series III–D
Head = 1.38 fr.

1	39.7	97.8	83,360	70.3	85.4	55.2	230	70.5
2	44.6	97.9	82,290	66.3	82.0	61.7	238	81.5
3	50.0	98.1	106,050	74.2	92.9	70.5	269	105.0
3*a*	50.4	97.8	110,700	70.8	88.2	71.1	255	96.0
4	53.4	98.0	110,710	72.2	91.3	74.5	265	108.0

Series III–E
Head = 1.49 fr.

1	39.6	98.2	76,660	75.7	93.6	53.8	238	74.0
2	44.2	98.2	88,920	71.4	90.3	60.6	246	86.0
3	49.5	97.8	107,430	70.3	88.6	69.3	259	104.0
3*a*	50.5	97.7	105,990	71.3	88.7	71.3	249	100.5
4	54.2	98.4	115,150	72.0	91.9	75.8	246	111.5

Series III–F
Head = 1.59 fr.

1	39.6	98.3	79,220	73.7	91.7	55.3	227	77.0
2	43.3	97.5	92,020	71.3	90.8	60.0	243	89.5
3	49.3	97.5	107,930	71.2	90.1	69.4	246	105.0
4	54.5	97.8	119,260	71.9	93.2	75.9	249	115.0
5	58.7	98.3	—	—	—	78.4	261	102.5

TABLE III

Average Efficiencies

Series	Overall	Transmission
III–*A*	72.4	91.0
III–*B*	69.2	86.8
III–*C*	69.7	87.6
III–*D*	70.7	88.0
III–*E*	72.1	90.6
III–*F*	72.0	91.4

Average Coefficient, all Series, 258.

The values given in the tables are plotted in Fig. 3. It may be seen from these curves that the coefficient rises with increase in temperature gradient. This rise may be due in part to the fact that ebullition becomes more vigorous as the temperature rises and consequently the surface of evaporation and the area of the

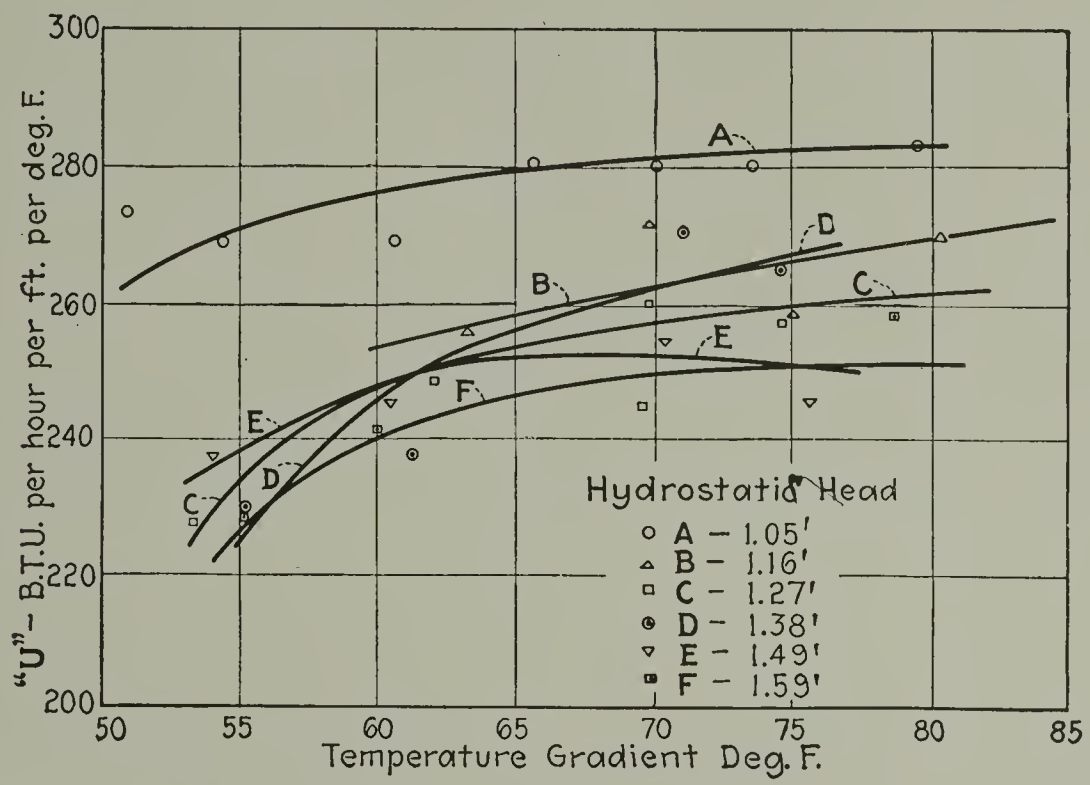


FIG. 3

heating surface increase. Moreover,—and this is perhaps still more significant—the film of liquid or vapor clinging to the inner surface is more effectively scoured off by the shearing action of the convection currents. A summary of the results given above is made in Table IV.

TABLE IV

HEAT TRANSMISSION SUMMARY FOR CAST-IRON KETTLE

Series No.	Hydrostatic Head (Ft.)	Temperature Gradient		
		60 Deg. F.	70 Deg. F.	80 Deg. F.
		Coefficient *U*		
3–*A*	1.05	276	280	280
3–*B*	1.16	252	262	271
3–*C*	1.27	246	258	261
3–*D*	1.38	245	264	266
3–*E*	1.49	248	253	252
3–*F*	1.59	240	250	251

Transmission in Enamel-Lined Evaporators

The kettle used in this series was one manufactured by the J. L. Mott Iron Works, described as the 54-gal. enamel-lined 111-X. Except for minor details the set-up and methods of measurement were the same as followed in the preceding work. The arrangement is shown in Fig. 2 and dimensions and wall thickness in Fig. 1. As might be expected, the rate of heat flow is low and high steam pressures were needed to keep the evaporating water at the boiling point.

TABLE V

Heat Transmission in Enameled Kettle

Series 4–1B

Head = 1.16 ft.

Run No.	Abs. Steam Press. (Lb. per Sq. In.)	Water Evaporated, Lb.	Temp. Grad. Deg. F.	*U* Steam to Water
1	40.2	20.0	57.4	67
2	46.6	23.5	65.1	70
3	50.5	26.0	72.0	70
4	54.9	27.0	74.7	70
5	59.5	30.5	79.7	74
Mean				70

Results are remarkably constant and they doubtless may be accepted as standard for apparatus of the kind. Recently Poste [4] in discussing enameled cast-iron kettles ranging in thickness from one-half to one inch gave values for the overall coefficient ranging from 52 to 60. It should be noted that our kettle is only one-half inch in thickness and also that Poste does not mention the thickness of enamel lining.

Film Coefficients

No direct measurements were made on film conductivities, desirable as they might be. It is interesting to note, however, that by substituting known or approximate values in the equation

$$\frac{1}{H} = \frac{1}{h_1} + \frac{L}{k_2} + \frac{1}{h_3}, \tag{4}$$

the value of h_1 may be calculated. If H is 260, h_3 the film between steam and the metal 2200 as suggested by McAdams, and k_2 the conductivity of one-half inch of cast iron is 864, then h_1 the con-

[4] *Ind. Eng. Chem.*, 16, 463 (1924).

ductivity of the film between the metal and boiling water is 456. In the case of the enameled kettle no data for conductivity of the special glass are available and so that for flint glass (0.3) is used. On substituting in the formula as before we get 249 for h_1. Naturally we should expect a lower figure than in the other case because of the considerably lower speed of the convection current.

In the use of any of the common metals such as iron, copper or aluminum for apparatus of this kind it is obviously difficult to maintain a chemically clean surface. Consequently the accuracy of water or steam film conductivity data is vitiated by indefiniteness of the cleanliness factor, for the oxide film must of course exert a marked influence on transmission. Indeed, in a later paper we shall show that in the case of a copper kettle a film of oxide serves as a material insulator, our results being directly comparable with those obtained by Pridgeon and Badger with tarnished evaporator tubes.

Location of Air Pockets

As a means of locating air pockets in the steam jacket thermometers inserted in brass stuffing boxes distributed as shown in Fig. 1 were provided since variations in temperature indicate the presence of non-condensible gases. Readings were averaged and corrected and the results are tabulated in Table VI.

TABLE VI

Variation in Jacket Temperatures

(See Fig. 3)

Series III–A

Run No.	t_7	t_8	t_9	t_{10}	$t_7 - t_8$	$t_7 - t_9$	$t_7 - t_{10}$
1	262.0	261.1	261.5	260.1	.9	.5	1.9
1*a*	265.1	263.8	264.2	262.2	1.3	.9	2.9
2	271.4	271.4	272.2	269.6	0	−.8	1.8
2*a*	276.8	275.9	275.9	274.8	.9	.9	2.0
3	280.6	279.3	279.3	277.7	1.3	1.3	2.9
3*a*	281.1	—	—	—	—	—	—
4	284.4	282.9	282.4	280.9	1.5	2.0	3.5
5	290.3	289.2	289.4	284.7	1.1	.9	5.6
Series No. III–B							
1	266.2	262.9	266.0	263.5	3.2	.2	2.7
2	273.2	272.5	273.2	261.4	.7	0	1.8
3	280.2	279.0	279.1	278.1	1.2	1.1	2.1
3*a*	281.3	—	—	—	—	—	—
4	286.9	284.9	284.7	284.2	2.0	2.2	2.7
5	290.7	289.4	289.6	289.0	1.3	1.1	1.7
5*a*	291.0	289.9	289.2	285.4	1.1	1.8	5.6

Series No. III–C

1	263.7	262.6	263.1	261.3	.9	.6	2.4
2	271.9	271.8	272.3	270.7	.1	−.4	1.2
3	280.9	279.5	279.1	278.4	1.4	1.8	2.5
3*a*	280.6	—	—	—	—	—	—
4	289.9	284.2	283.6	278.8	5.7	6.3	11.1

Series No. III–D

1	266.5	264.6	264.4	265.1	1.9	2.1	1.4
2	273.0	272.5	271.8	271.0	.5	1.2	2.0
3	281.8	280.0	279.1	278.8	1.8	2.7	3.0
3*a*	281.8	—	—	—	—	—	—
4	285.8	283.8	282.7	282.7	2.0	3.1	3.1

Series No. III–E

1	265.1	263.7	262.8	258.4	1.4	2.3	6.7
2	271.9	271.4	271.0	266.9	.5	.9	5.0
3	280.6	279.3	278.8	274.3	1.3	1.6	6.9
3*a*	282.0	—	—	—	—	—	—
4	287.1	284.5	283.5	279.5	2.6	3.6	7.6

Series No. III–F

1	265.5	263.8	263.5	262.4	1.7	2.0	3.1
2	271.2	270.5	270.1	269.6	.7	1.1	1.6
3	280.6	279.3	279.0	278.2	1.3	1.6	2.4
4	287.1	285.3	284.5	284.0	1.8	2.6	3.1
5	289.6	288.9	288.3	288.1	.7	1.3	1.5

It is evident that except for a few cases the temperature variation was not great and it is probable that no air pockets of great size or permanence were present. Under other conditions, however, it is conceivable that non-condensible gases might collect and it is of course advantageous to have available means for venting them.

The following estimate of the final accuracy of results is reached after an examination of the possible magnitude of errors in reading thermometers and gauges and making weighings: for overall efficiencies 0.5 per cent; transmission efficiencies 1.5 per cent; and for the transmission coefficient 2.5 per cent.

Summary

The values of the transmission coefficients from steam to boiling water in cast iron and enameled cast-iron kettles of a widely used type have been determined as 260 and 70 respectively. The coefficient from steam to air which represents radiation loss is 5 when no

air drafts interfere; with moderate circulation this may be increased twenty-five per cent.

Increase in temperature gradient causes a rise in the value of the transmission coefficient although in the case of walls of high resistance the effect is very small. Increase in hydrostatic head decreases the coefficient and this effect is least marked when large gradients are employed.

TYLER ELECTRIC SILICA STILL

By J. C. OLSEN, W. LINDENTHAL and I. SHERMAN

Read at the Denver Meeting, July 17, 1924

The still described in this paper was designed and constructed by Mr. S. L. Tyler of the Thermal Syndicate. With the exception of the heating element it is constructed entirely of silica, including the condenser. As the heating element is enclosed in a silica tube, acids of any concentration may be distilled in the apparatus.

The still is composed of three units so connected that the acid may be fed into the first unit, overflow into the second, and then into the third unit from which the final excess drips. The three units may therefore be operated continuously, the impurities which accumulate in the still being removed in the drip from the third unit. The working capacity of each unit is about 1.8 liters of boiling liquid. The design of the single unit is shown in Fig. 1. The method of connecting the three units is shown in Fig. 2. The distillate may be collected in a manifold leading to a single condenser as shown in Fig. 3 or a silica condenser may be connected to each unit as shown in Fig. 4.

The construction and location of the electric heating element is shown in Fig. 5. A small bore Vitreosil tube is inserted through an asbestos rope about one and a half inches thick, the rope being loosely wound and readily compressible to the diameter of the heater tube ($1\frac{1}{4}$ inches). The resistance wire (Chromel "A"—No. 19) has been passed through the center tube and then wound in a helix around the bottom of the asbestos rope for a distance of about 6 inches. Each unit consumes about 0.7 kw. at 110 volts. As the current through each heating coil is 7 amperes the three units in parallel use 21 amperes of current. According to the Hoskins wire table No. 19 wire with 6.8 amperes flowing gives a temperature of 1200 degrees F. when the wire is wound in a helix. This must therefore be approximately the temperature given by the heating elements. The upper part of the asbestos rope is left loose so as to form a seal and keep heat from escaping through the top of the heater tubes. This unit heats water to boiling in about twenty minutes.

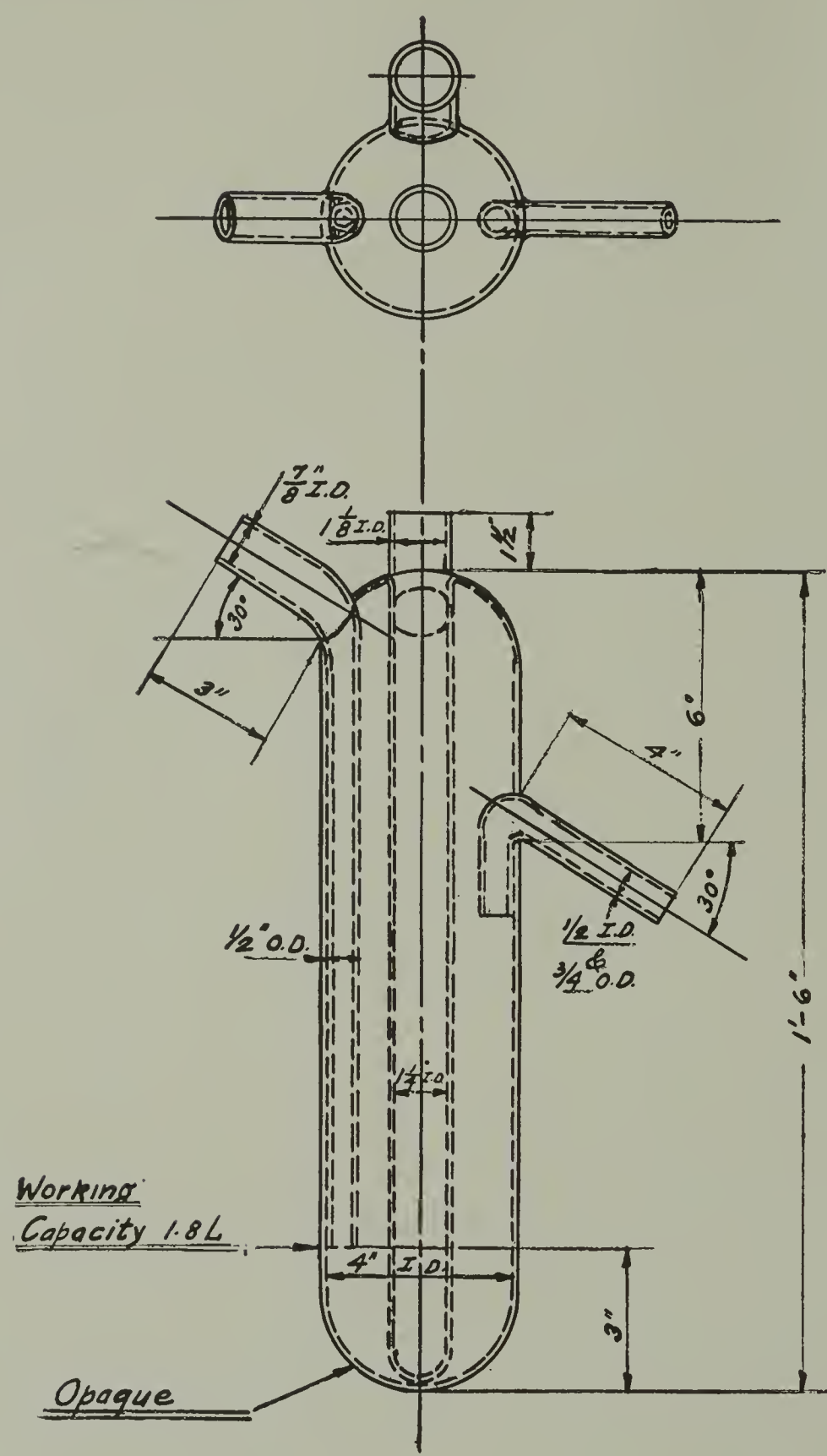


FIG. 1. Design of single unit.

Fig. 4 shows the heating elements in place and wired through an ammeter to the terminals of the 110-volt circuit. This figure also shows the feed consisting of a large dropping funnel as well as the overflow.

Effective insulation was necessary to conserve electric current. Fig. 3 shows the first insulation used which consisted of ordinary

shredded magnesia asbestos. Each unit is coated with an initial layer of about a half inch of the asbestos, and then corrugated asbestos paper is wrapped around the unit to give an insulating air space. Whereupon another layer of approximately $\frac{3}{8}$ inch of asbestos is coated on.

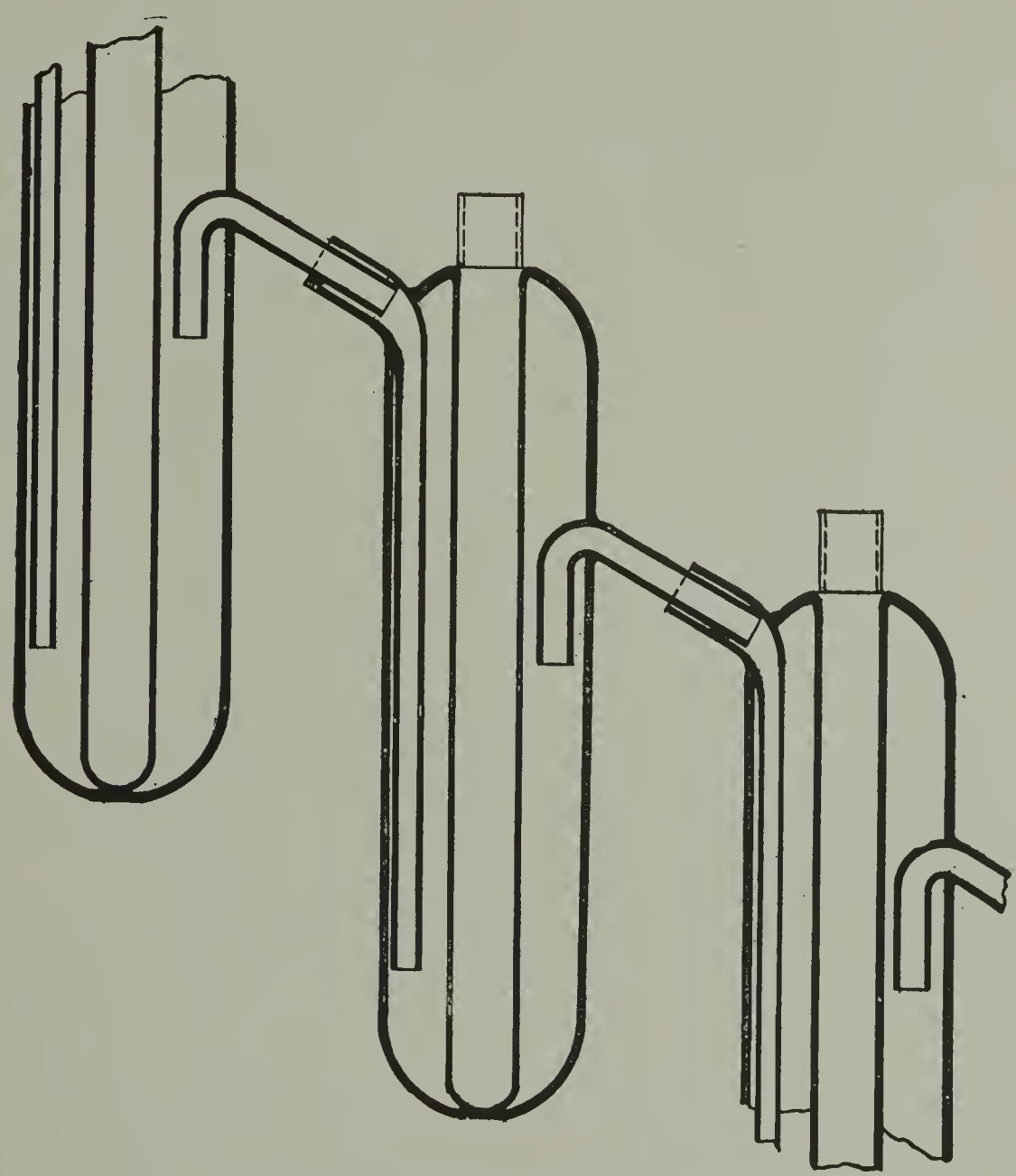


FIG. 2. Method of connecting units.

Fig. 6 shows the still boxed in and each unit surrounded by coarsely ground Sil-O-Cel C_3, which proved to be a much more efficient insulator.

The joints between the stills and the condenser were made tight by means of asbestos wet with sodium silicate.

A number of runs were made with distilled water to ascertain the thermal efficiency and capacity of the still. In each case the water was heated to boiling, the feed water started and a state of

equilibrium reached before beginning to take observations. Current and voltage readings were taken at intervals of 5 minutes, the temperature of the feed water noted, and the amount of water

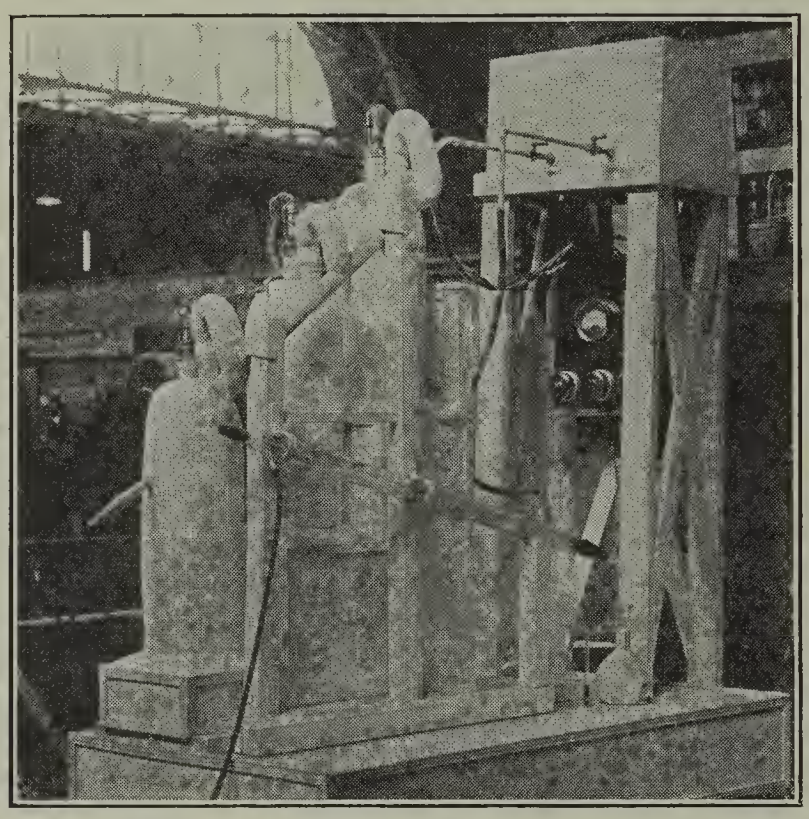


FIG. 3. Units connected to manifold leading to single condenser.

distilled. The efficiency of the still was calculated from the heat of vaporization of the water and the heat equivalent of the electric current used assuming one watt hour to be equal to 860 calories.

The results of 5 runs are given in the following table:

	Run No. 1	Run No. 2	Run No. 3	Run No. 4	Run No. 5
Time	30	30	30	30	30
Volts	107	107	106	106	105
Amperes	20.9	20.7	20.7	21.0	20.8
Feed water temp. (°C.)	22	22	13	23	23
Gm. water distilled	1,333	1,315	1,243	1,298	1,297
Output (calories)	816,000	806,000	775,000	795,000	795,000
Input (calories)	962,000	952,000	941,000	955,000	940,000
Efficiency (%)	85.0	84.8	82.2	83.6	84.5

The cost of the current per liter of distilled water would be:

Cost of electricity per kw. hr.	8 cents	5 cents	3 cents
Cost per liter distilled	6.7 "	4.2 "	2.5 "

In order to ascertain the amount of water which spattered over into the distillate a 10 per cent salt solution was used to feed the still and the amount or salt in the distillate determined. 100 c.c. of the distillate was found to contain 3 mg. of salt. This would indicate spattering equal to .03 per cent.

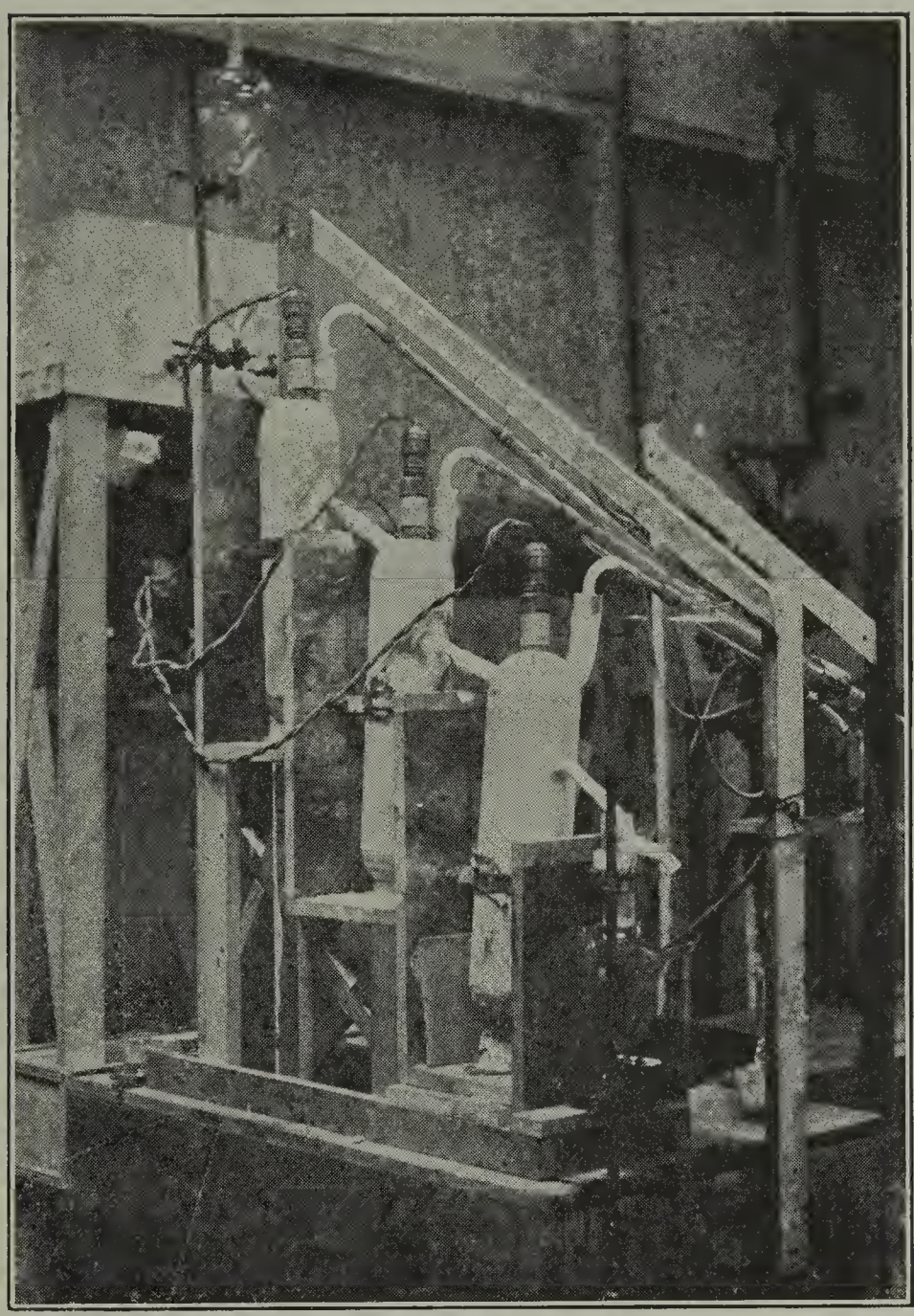


FIG. 4. Condensers connected to each unit.

Several runs were made with the still without any insulation and the efficiency calculated as before from the amount of water distilled. The results were as follows:

	Run No. 6	Run No. 7	Run No. 8
Time of run (min.)	30	32	30
Volts	105	105	105
Amperes	20.4	21.0	20.5
Gm. distilled	1,105	1,210	1,100
Feed water temp. (°C.)	13	14	14
Input (calories)	921,000	1,012,000	926,000
Output (calories)	689,000	745,800	686,000
Efficiency (%)	74.9	73.8	74.0
Av. Efficiency (%)			74.2

After insulating with Sil-O-Cel C_3 two runs were made to ascertain the efficiency of this insulation. They resulted as follows:

	Run No. 9	Run No. 10
Time of run	30	30
Volts	105	105
Amperes	21.3	21.0
Feed water temp. (° C.)	20	20
Gms feed added	1,200	1,400
Gms distilled	1,410	1,330
Output (calories)	852,000	825,000
Input (calories)	963,000	945,000
Efficiency (%)	88.4	87.6

Distillation of Sulphuric Acid

For distilling water it was found satisfactory to pack the joints with soft cotton cord packing covered with friction tape. For the acid distillation the joints were packed by inserting asbestos cord in the spaces between the tubes and then plastering a layer of

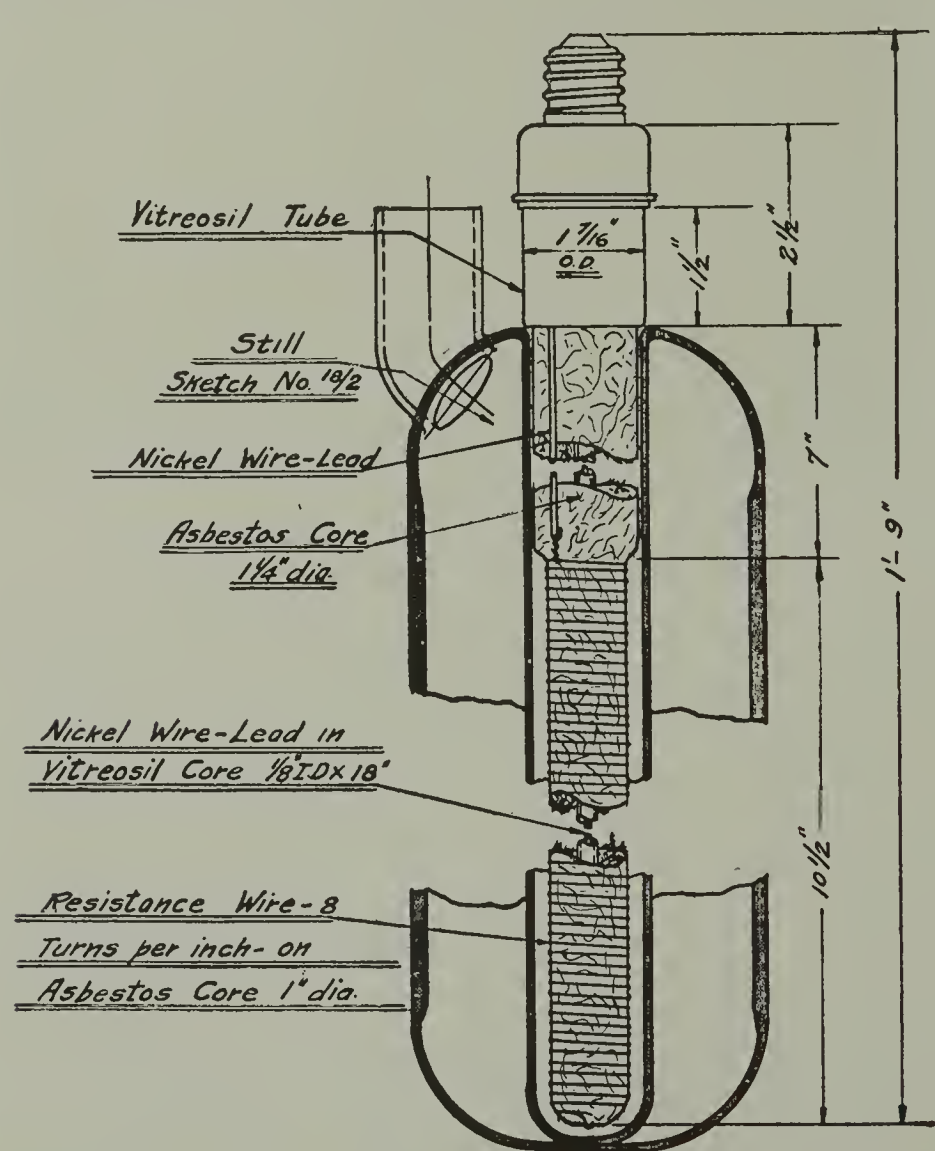


Fig. 5. Construction and location of electric heating unit.

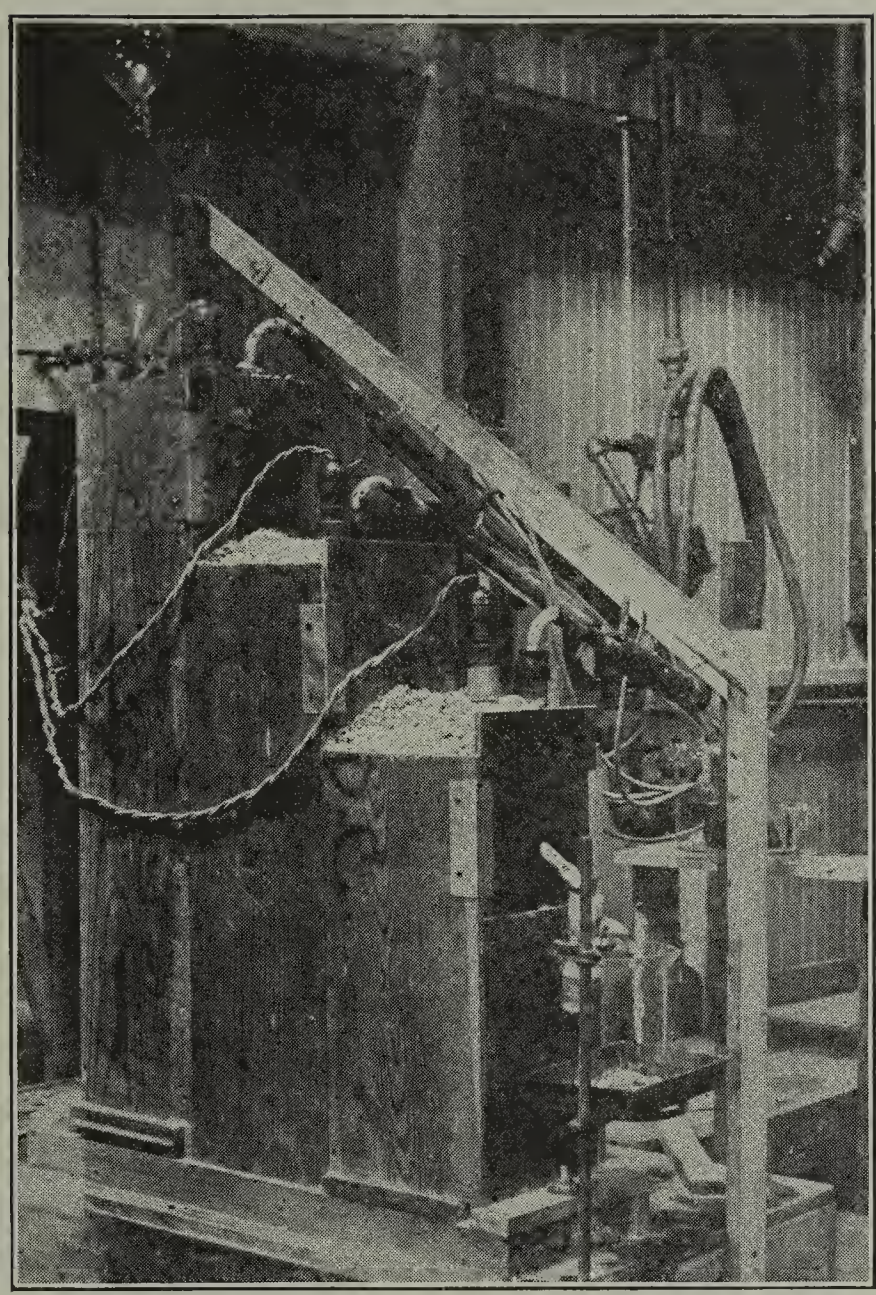


FIG. 6. Still boxed in and insulated with Sil-O-Cel.

shredded magnesia asbestos wet with dilute sodium silicate solution over the joint. Single condensers were used so that the distillate from each unit was collected separately. The acid used was 66° Baume commercial sulphuric acid. The distillate was absolutely clear and colorless. The following results were obtained:

It will be noted that the distillate from still No. 1 was small in amount and of very low specific gravity. It consisted almost entirely of water. The first still evidently served mainly as a heating unit. There was some tendency for the acid to spit back out of the inlet tube of still No. 1. This was no doubt due to the contact between the distillate feed acid coming into contact with the boiling acid in the still.

The distillate from the third still showed a higher concentration than from the second still. The average output is 2.68 pounds

acid per kw. hr., the output per hour is 6.03 pounds and per 24-hour day is 145 pounds.

	Run No. 11	Run No. 12	Run No. 13
Time of run (min.)	55	42	36
Volts	105	106	105
Amperes	21.0	21.0	21.0
Total input (kw. hr.)	2.02	1.55	1.40
Distillate from still No. 1 (c.c.)	140	72	36
(gm.)	152	79	41
Sp. gr. distillate No. 1	1.09	1.10	1.14
% acid distillate No. 1	10.6	11.7	16.0
Distillate from still No. 2 (c.c.)	620	480	450
(gm.)	1,120	878	824
Sp. gr. distillate No. 2	1.83	1.83	1.8
% acid distillate No. 2	95.3	93.8	93.33
Distillate from still No. 3 (c.c.)	610	525	460
(gm.)	1,135	964	845
Sp. gr. distillate No. 3	1.835	1.835	1.835
% acid distillate No. 3	97.8	97.9	97.4
Total acid distilled (gm.)	2,410	1,921	1,710
Total acid from stills No. 1, 2, 3 (gm.)	1,190	1,230	1,220
Per kw. hr. total input (pounds)	2.63	2.71	2.69
Pounds per hour	5.78	6.04	6.27
Av. % acid from 3 stills	91.2	92.4	93.5
Distillates Nos. 2 and 3 combined (gm.)	1,120	1,180	1,190
Per kw. hr. total input (pounds)	2.46	2.60	2.63
Av. % acid stills Nos. 2 and 3	96.5	95.8	95.5

Distillation of Nitric Acid

Commercial 42° Baume nitric acid was distilled in the same manner as the sulphuric acid. The distillate from still No. 1 was nearly always colored. The distillates from the other stills had only slight color, if any. The results of these runs are given in the following table:

	Run No. 14	Run No. 15
Time of run (min.)	55	30
Volts	106	106
Amperes	21.0	21.0
Total input (kw. hr.)	2.04	1.11
Distillate from still No. 1 (c.c.)	460	235
(gm.)	621	317
Sp. gr. distillate No. 1	1.35 (37.7° Be.)	1.35 (37.7° Be.)
% acid distillate No. 1	55.9	55.9
Distillate from still No. 2 (c.c.)	1,204	660
(gm.)	1,680	907
Sp. gr. distillate No. 2	1,375 (39.5° Be.)	1,375 (39.5° Be.)
% acid distillate No. 2	60.0	60.0
Distillate from still No. 3 (c.c.)	1,194	660
(gm.)	1,660	918

	Run No. 14	Run No. 15
Sp. gr. distillate No. 3	1,395 (41° Be.)	1.39 (40.5° Be.)
% acid distillate No. 3	64.2	62.7
Total acid distilled (gm.)	3,961	2,142
Total acid from all stills (gm.)	1,940	1,950
Per kw. hr. total input (pounds)	4.3	4.25
Pounds per hour	9.44	9.43
Av. % acid from all stills	61.2	60.4
Distillates Nos. 2 and 3 combined (gm.)	1,630	1,640
Per kw. hr. total input (pounds)	3.6	3.6
Av. % acid stills Nos. 2 and 3	62.0	61.2

The average output per kw. hrs. is 4.28 pounds, the output per hour is 9.43 pounds and per day of 24 hours is 226 pounds.

Increase of Electric Input

In the attempt to increase the capacity of the still new heating units were made up which converted more electric energy into heat. The old units were made of No. 19 Chromel "A" resistance wire, had a resistance of 15.1 ohms and consumed about 0.7 kw. at 110 volts. The new heating units were made of 33 ft. of No. 18 Chromel wire and consumed 8.25 amperes or about 0.91 kw.

The efficiency of the steel with the new units was tried out with water. In addition to a number of short runs a run of four hours was carried out with the following result. No readings were taken until equilibrium had been attained.

Time of run	4 hours
Volts (average)	101
Amperes (average)	20.7
Feed water temperature	18° C.
Grams water added	11,721
Grams water distilled	10,678

$$\text{Input} = 101 \times 20.7 \times 860 \times 4 = 7{,}176{,}000 \text{ calories,}$$

$$\text{Output} = 11{,}721(100 - 18) + 10{,}678(536) = 6{,}706{,}200 \text{ calories,}$$

$$\text{Efficiency} = \frac{6{,}706{,}200}{7{,}176{,}000} \times 100 = 93.5 \text{ per cent.}$$

The new units give a considerably higher energy efficiency than the old units.

A test was made to determine the amount of spattering with the new units by distilling a 10 per cent salt solution. 100 c.c. of the

distillate was found to contain 10.4 mg. salt. This would indicate spattering equivalent to 0.1 per cent which is somewhat higher than with the old units.

A test was also made to ascertain the amount of spattering when distilling sulphuric acid by distilling an acid which contained 5 per cent ferrous sulphate. Only slight traces of iron could at times be detected in the distillate while in a number of runs no iron at all could be found.

Conclusion

The silica still described utilizes electric energy with an efficiency as high as 92 per cent.

The three units described may be used to produce distilled sulphuric or other acids of very high purity, the output in the case of sulphuric acid being 145 lbs. per 24 hours.

Sulphuric acid may be concentrated in this still to over 97 per cent.

CONCENTRATING DILUTE NITRIC ACID

A Study of the Relation between the Vapor and Liquid Phases in the Distillation of Nitric Acid-Water Solutions, and of Nitric Acid-Sulphuric Acid-Water Solutions

By CLIFFORD D. CARPENTER AND JOSEPH A. BABOR

Read at the Denver Meeting, July 17, 1924

With the discovery of nitroglycerine in 1862 and the later development in the production of nitrated products came the first great demand for highly concentrated nitric acid. At that time the manufacture of nitric acid of high concentration was accomplished by treating sodium nitrate with concentrated sulphuric acid. Although many other processes have been developed, this process which dates back to Glauber in 1648 is still the "backbone" of the nitric acid industry.

It was immediately recognized that the demand would soon overtax the supply, and a solution of the problem became imperative. This resulted, first, in efforts to produce an acid of high concentration by other means, and, second, to recover and concentrate the dilute acids from spent liquors. Very little attention had been given to the recovery of "spent acid" or the dilute acid produced simultaneously with the manufacture of the more concentrated acids.

The attempt to produce economically a concentrated acid by other means has not met with success. Recently, however, satisfactory progress has been made in the development of methods for the recovery of the "spent acid" and to-day, together with the concentrating of the dilute acids produced synthetically, the concentrating of dilute nitric acid solutions is a major industrial operation. Rather complete bibliographies of the scientific and patent literature on the production and recovery of nitric acid are given by Boyce,[1] Creighton [2] and Cottrell.[3]

A review of the literature shows that the concentrating of dilute nitric acid has been attempted along two lines, the neutralization of the acid, evaporation and recovery as a nitrate from which concentrated nitric acid can be liberated by treatment with concentrated sulphuric acid, and by fractional distillation. In the early years of the war the Central Powers recovered the nitric acid from dilute

solutions by treating them with soda ash to produce sodium nitrate which was recovered by evaporation of the solution. This nitrate was then treated with sulphuric acid in order to produce concentrated nitric acid. In 1918 Cocking [4] employed ammonia instead of soda ash. Such methods, however, involve the consumption of such great quantities of raw materials that the cost, when compared with other methods, becomes economically prohibitive. This, therefore, has left open only the development of distillation methods for the concentrating of dilute solutions of nitric acid.

Although the boiling point of nitric acid is 14 deg. C. below that of water, it is well known that a highly concentrated acid cannot be produced by fractional distillation, for a solution of 68 per cent concentration has a maximum boiling point, i.e., a minimum vapor pressure. The limit of concentration of a dilute solution by simple fractionation is, therefore, 68 per cent. The addition, however, of sulphuric acid to such solutions alters completely the nature of the vapor phase. The vapor becomes richer in nitric acid and solutions of very low nitric acid content yield a vapor which approaches 100 per cent nitric acid as the concentration of the sulphuric acid becomes high. The sulphuric acid is called a water binder. Many investigations have been carried on in an attempt to find more efficient or cheaper water binders. Frischer [5] has proposed the use of other acids such as arsenic, phosphoric, polysulphates, etc. Bocters [6] has proposed salts which form hydrates such as calcium and magnesium chlorides, sodium and calcium sulphates, and various nitrates. Creighton and Smith [7] studied the effect of potassium acid sulphate upon dilute solutions of nitric acid, and found that although the maximum boiling point was raised the composition of the vapors from such solutions was not changed.

In general no other water binder has been found to be more efficient than sulphuric acid. All others have disadvantages such as not being so available, or involving mechanical handicaps and hazards not experienced with the use of sulphuric acid. Another important advantage of sulphuric acid as a water binder is the relative ease with which it can be recovered, i.e., by simple evaporation.

Although some consideration has been given to concentrating dilute solutions of nitric acid by "preconcentrating" the dilute solutions to 55 or 65 per cent concentration, before addition of sulphuric acid for the final so-called "superconcentrating," it has proved more practical to add the water binder to the dilute solution

for the first fractionation, and finally recover the sulphuric acid by evaporation. The main advances which have been made in the efficiency of this process have been mechanical, such as the construction of the towers, methods of heating, adding materials, etc. An idea of these operations may best be gained by a review of the patents. Among the most efficient are those of Pauling [8] and Zeisberg.[9]

A quotation of the first claim from each gives a general idea of the process. Pauling accomplishes the concentration by "passing aqueous nitric acid in admixture with a suitable dehydrating agent against a countercurrent of hot gaseous medium composed largely of steam, and so regulating the conditions of the operation that vapors of highly concentrated nitric acid are obtained, while the dehydrating agent takes up and retains substantially all the water of the aqueous nitric acid." Zeisberg's claims begin as follows: "The process which comprises subjecting nitric acid and sulphuric acid containing not less than 64 per cent of sulphuric acid and from 3 to 25 per cent of nitric acid to a hot gaseous current, carrying away the nitric acid vapors and condensing the same."

This general method has proved very efficient in the recovery of such dilute acids as (1) T.N.T. spent acid, 4.5 per cent nitrogen acid content, (2) Nitroglycerine spent acid, 8.5 per cent nitrogen acid content, (3) Nitrocotton spent acid, 20 per cent nitrogen acid content, (4) Synthetic acid from arc process, 35 per cent nitrogen acid content and (5) Synthetic acid from ammonia process, 55 per cent nitrogen acid content.

As in the case of many industrial operations, great advances have been made by long experience with the industrial operation, yet back of the manipulations there are many steps involved which are not definitely known. In fact the efficiency of the present-day practice in concentrating dilute solutions of nitric acid seems to leave little opportunity for improvement. This is likely due to the fact that in a properly constructed tower conditions exist for nearly ideal fractionation.

It is highly desirable, however, to know the exact relations between the vapor phase and the liquid phase for all solutions. Recently some careful experimental work has been carried out to learn the exact relation between these phases. In 1919 Carpenter and some of his students carried out preliminary experiments in an attempt to develop a method by which the rate of concentrating of nitric acid by distillation could be carried out without

fractionation. Later Carpenter and Babor [10] improved the preliminary work and developed a satisfactory method. While this work was in progress two papers, one by Pascal [11] and one by Berl and Samtleben,[12] appeared and gave experimental data on the relation of the two phases of dilute nitric acid solutions. In a second paper Carpenter and Babor [13] corrected the experimental data in their first paper, extended the work and made a critical comparison between their work and that of Pascal and of Berl and Samtleben. Pascal [14] and Berl and Samtleben [15] have since reported further experiments on the ternary system, nitric acid-sulphuric acid-water.

After considering the success of the method developed by Carpenter and Babor and the nature of the results obtained in the work on concentrating dilute nitric acid solutions, it seemed advisable to extend the work to acids of higher concentrations, and to study the ternary system nitric acid-sulphuric acid-water in the same manner.

Apparatus

The apparatus illustrated in *a*, *b* and *c*, Fig. 0, are sketches of the apparatus used by Carpenter and Babor, by Pascal, and by Berl and Samtleben respectively. Those used by Pascal and by Berl and Samtleben are included for purposes of comparison.

The main points of difference lie in the precautions taken to prevent fractionation and superheating of any portion of the flask containing the distilling liquids. In *a*, heat is applied equally about the containing flask and the delivery tube through which vapors leave, by submerging the flask in a vigorously stirred liquid bath. In both *b* and *c* an air bath is used. In *c* a thermometer hangs directly into the vapors above the boiling liquid, while in *b* two thermometers and an aspirator tube are suspended in the vapor and boiling liquid. It is well known that an air bath cannot be kept uniformly heated. It is also self-evident that superheating can take place by the use of a sand bath or other local applications of heat. It is further evident that the thermometers and the neck of the distilling flask will give considerable lag when the temperature of the air bath changes and thus will furnish surfaces of varying temperatures which must cause fractionation. Although these results are easily anticipated, it is not necessary to accept the anticipation until proven by experiment. This can be readily recognized by referring to discrepancies in experimental data as shown later in this paper.

Chemicals Used

Nitric Acid: The nitric acid used in the lower concentrations was the C. P. grade, redistilled in an all Pyrex distilling apparatus. After the resulting acid was cooled, filtered air was bubbled through it to remove as far as possible any trace of NO_2. The acid thus produced, approximately 68 per cent, was stored in glass-stoppered bottles that were kept in the dark to prevent the slow decomposition caused by exposure to the light.

The nitric acid in the higher concentrations was made by distilling fuming nitric acid and finally freeing it from oxides of nitrogen by bubbling air through it while cooling from 40 to 20 deg. C. The resulting acid was practically free from nitric oxide and had a very pale straw color. Analysis showed it to be 92.26 per cent HNO_3 with less than 0.02 per cent N_2O_3. This acid was stored in amber colored glass-stoppered bottles in a cold dark place.

An attempt was made to produce nitric acid nearer 100 per cent concentration by the following method: Fuming nitric acid containing a considerable amount of NO_2 was electrolyzed in a cell as shown in Fig. 1. The neck of the flask was allowed to heat up so as to facilitate the escape of the reduction products of the nitric acid at the negative electrode. The bottom of the flask was kept cold by means of an ice bath. The electrodes were of platinum, sealed in glass tubes as shown in the figure. After 12 hr. the acid, except in the neighborhood of the negative electrode, became colorless. The current was turned off and the liquid in the neck of the flask syphoned off. The residual acid was colorless, gave no test for nitrous acid, and fumed in the air. It was immediately stored in a cool dark place. After 24 hours it had become amber yellow in color, and gave a decided test for nitrous acid.

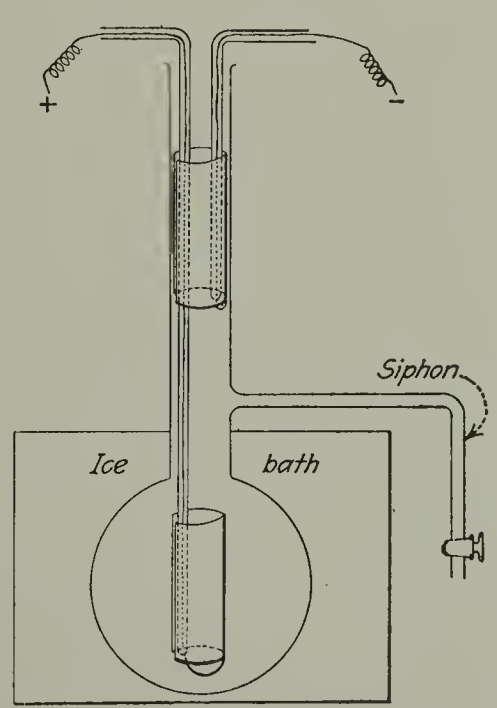


Fig. 1. Electrolytic Cell for Making 100 Per Cent HNO_3

Küster and Münch,[16] who prepared absolute nitric acid by fractional crystallization at − 41.3 deg. C., found that on melting the pure acid it became yellow, showing that 100 per cent nitric acid exists only in the solid state, *i.e.*, below − 41 deg. C., decomposing above

this temperature. Berthelot [17] found that 100 per cent nitric acid decomposes slowly according to the equation

$$2HNO_3 \rightleftharpoons 2NO_2 + O + H_2O$$

The decomposition, however, is never complete due to the presence of water, which probably forms hydrates which are more stable than the HNO_3. Veley [18] suggests that perhaps the HNO_3 is associated and the equilibrium is $(HNO_3)_n \rightleftharpoons nHNO_3$, similar to sulphuric acid. The instability, therefore, of concentrated nitric acid made it impossible to carry on experimental work at the high temperatures used in this work.

Sulphuric Acid: The sulphuric acid used for making up the distilling mixtures was Highest Grade H_2SO_4, free from chlorides and nitrates.

Sodium Hydroxide: The sodium hydroxide used for making up the standard solution for titrating was purified by making up a saturated solution of C. P. NaOH, was cooled and then filtered through hardened filtered paper. Distilled water, free from CO_2, was used in diluting the saturated solution to 0.1N. This was standardized against Bureau of Standards Benzoic Acid.

Water: All water used in diluting the acid was redistilled.

Experimental Procedure

A quantity of nitric acid-water solution, or of nitric acid-sulphuric acid-water solution of known composition was weighed into a large Pyrex distilling flask at the beginning of each experiment. The flask was then mounted on a stand which could be lowered into and clamped onto the bottom of a large copper pot which was used as a bath container, while the delivery tube was passed through a one hole stopper which fitted into an outlet in the bottom of the pot. The bath liquor, a solution of calcium chloride, was added until the top of the delivery tube was well covered. Using calcium chloride solution as the bath liquor, the maximum temperature attainable with safety was 135 deg. C. For the higher temperatures required in the ternary system it was found that the addition of glycerine up to 40 per cent by weight would permit heating the bath up to 180 deg. C. The inner tube of the condenser was then sealed to the end of the delivery tube. All experiments were carried on at atmospheric pressure. No runs were made except on days when the atmospheric pressure measured about 760 mm.

The temperature of the bath was then raised until a steady distillation took place. The distillate was collected in small weighed flasks, shown in Fig. 0 *a*, in portions approximately 50 g. each. These fractions were analyzed by titrating with standard sodium hydroxide solution.

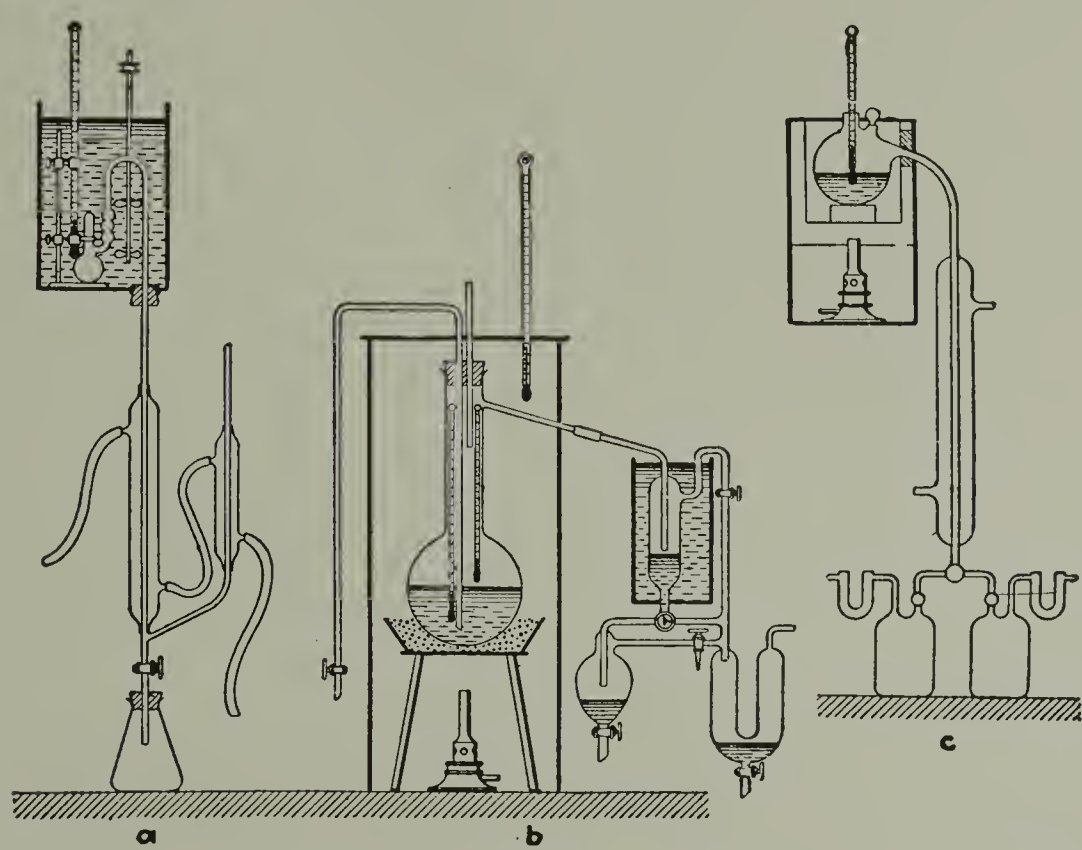


FIG. 0. Apparatus Used.

When strong nitric acid or mixtures of nitric acid-sulphuric acid-water were subjected to distillation and vapors of high nitric acid content were produced, i.e., 75 to 100 per cent, ice water was circulated through the condensers.

The fractions of high nitric acid content were diluted to a convenient volume and an aliquot part taken for titration. These fractions were also analyzed for nitrous acid, using standard permanganate solution. The fractions containing nitric oxides required special precautions to be taken while diluting to convenient volume in order to prevent loss. The dilution was made in a freezing bath to minimize the effect of the heat of dilution on the volatility of the nitric oxide. Freshly cooled distilled water was used for diluting in order to avoid the oxidation of the nitric oxide to nitric acid by the dissolved oxygen which is ordinarily present in appreciable amounts in distilled water that has been standing in contact with air. The cold diluted solutions were then slowly brought to room temperature and diluted to final volume.

Tests were continually made for sulphuric acid in the distillates.

Experimental Data

The experimental work was carried out in two parts. The first part is concerned with the higher concentrations in the binary system nitric acid-water, and the second with a complete survey of the ternary system nitric acid-water-sulphuric acid.

Part I. System Nitric Acid-Water

Nitric Acid-Water: Previous work by Carpenter and Babor covered the binary system nitric acid-water for acids below 68 per cent nitric acid concentration. This work on the binary system has been extended to acid solutions between 70 and 92 per cent nitric acid concentration. Four runs were made and the results are given in Table I.

TABLE I

Distillation Between 70 and 92 Per Cent Nitric Acid

Run 1. Bar. = 759.0 mm.

Weight of Residue, Grams	Weight of Total Distillate, Grams	Weight of Total HNO_3 Distilled, Grams	Total Per Cent Distilled	Strength of Residue, Per Cent	Temperature of Bath, deg. C.
223.072	0.0	0.0	0.0	92.27	
206.93	16.140	15.967	7.24	91.74	93 – 97.9
180.310	42.762	42.153	19.17	90.76	97.9–100
157.316	65.756	64.689	29.48	89.71	100 –101.2
134.084	88.987	87.419	39.89	88.30	101.2–102.2
109.355	113.720	111.400	50.98	86.34	102.2–107
91.069	132.003	129.00	59.17	84.34	107 –111

Run 2. Bar. = 758.6 mm.

242.754	0.0	0.0	0.0	86.27	
210.391	32.363	31.210	13.33	84.71	105 –108.2
185.230	57.524	55.191	23.70	83.26	108.2–111.6
160.826	81.928	78.195	33.75	81.59	111.6–114.5
145.183	97.571	92.690	40.20	80.40	114.5–115.0

Run 3. Bar. = 761.7 mm.

242.377	0.0	0.0	0.0	82.70	
223.602	18.775	17.638	7.75	81.75	112 –113.1
195.563	46.815	43.596	19.32	80.22	113.1–115.1
169.576	72.801	67.089	30.04	78.64	115.1–116.8
143.638	98.739	89.762	40.74	77.05	116.8–117

Run 4. Bar. = 763.0 mm.

302.700	0.0	0.0	0.0	78.60	
270.426	32.274	28.687	10.66	77.37	115.2–117.1
231.055	71.645	63.097	23.67	75.66	117.1–118
193.200	109.500	94.750	36.17	74.10	118 –119
145.683	157.017	132.755	51.87	72.19	119 –119.5
95.349	207.351	170.970	68.50	70.21	119.5–120.5

These results are then expressed in the curves 1 (up to point A), 2, 3 and 4, in Fig. 2. A composite line which expresses the change in a continuous distillation from 92.265 per cent concentration down to one of 70.214 per cent concentration is made by translating the values in Runs 2, 3 and 4 into such terms that they may be plotted as extension of curve 1.

In order to translate the values in Run 2 so that they may be considered as an extension of curve 1, the ordinate corresponding to 86.27 per cent concentration on curve 1 is noted. This is 51.2 per cent distilled. The values for per cent distilled in Run 2 are then multiplied by 48.8 and the product is added to 51.2. This gives the new points on the ordinate for each value. The results follow.

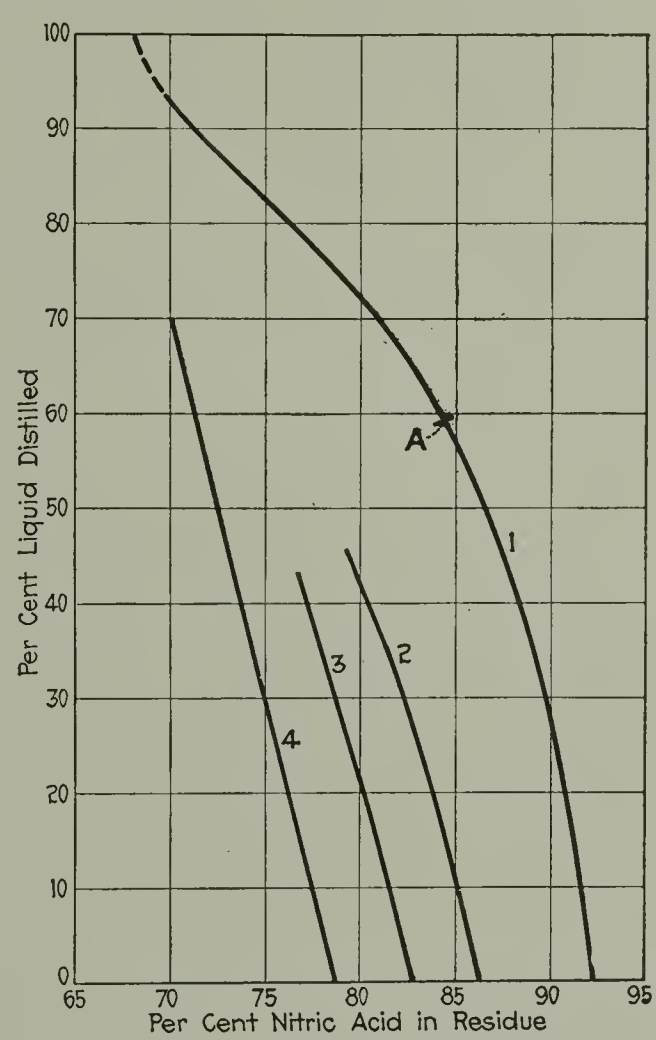


FIG. 2. Distillation of HNO_3 between 70 and 92 Per Cent

Total Per Cent Distilled	Strength of Residue	Position on Ordinate
0.00	86.27	51.2 + 0.00 = 51.2
13.33	84.71	51.2 + 6.51 = 57.71
23.70	83.26	51.2 + 11.56 = 62.76
33.75	81.59	51.2 + 16.47 = 67.67
40.20	80.40	51.2 + 19.61 = 70.81

Run 3 was translated by multiplying each per cent distilled by 35.45 and adding the product to 64.55.

Total Per Cent Distilled	Strength of Residue	Position on Ordinate
0.00	87.70	64.55 + 0.00 = 64.55
7.75	81.75	64.55 + 2.75 = 67.50
19.32	80.22	64.55 + 6.85 = 71.40
30.04	78.64	64.55 + 10.64 = 75.19
40.74	77.05	64.55 + 14.44 = 78.99

Run 4 was translated by multiplying each per cent distilled by 24.60 and adding the product 75.40.

Total Per Cent Distilled	Strength of Residue	Position on Ordinate
0.00	78.60	75.40 + 0.00 = 75.40
10.66	77.37	75.40 + 2.62 = 78.02
23.67	75.66	75.40 + 5.83 = 81.22
36.17	74.10	75.40 + 8.90 = 84.30
51.87	72.19	75.40 + 12.76 = 88.16
68.50	70.21	75.40 + 16.85 = 92.25

Although a slight error is involved due to the decomposition of the stronger acids, this proved to be so small that the value of the results is not impaired, for the first fraction from the 92.2 per cent acid contained only 0.05 per cent N_2O_3 content and the second fraction less than 0.02 per cent; the first fraction from the 86.27 per cent acid 0.03 per cent; the first fraction from the 82.70 per cent acid 0.02 per cent, and all other fractions less than 0.01 per cent.

When the composite curve 1 is laid out on large co-ordinate paper it is a simple matter to read directly the change in concentration in the residue between any two points on the per cent distilled ordinate. It is also a simple matter to calculate from these data the rate at which the concentration of the distillate changes, and with these results to finally plot the rate of change in concentration of distillate against the rate of change in concentration of the undistilled residue. It is then possible to calculate the vapor in equilibrium with a given concentration of nitric acid in the residue. This was done and the results have been given in column 2, with the results of Carpenter and Babor, column 1, of Berl and Samtleben, column 3, and of Pascal, column 4, in Table II.

The results obtained by Pascal and by Berl and Samtleben are given for comparison. Finally, the results in columns 1 and 2, Table II, are plotted as a continuous curve in Fig. 3. Pascal's values are indicated by small squares. Those of Berl and Samtleben by small circles with arrows attached to show how they fall with respect to the curve which is determined by the solid dots representing the results previously obtained by Carpenter and Babor and

TABLE II

VAPOR IN EQUILIBRIUM WITH BOILING NITRIC ACID SOLUTIONS

Strength of Acid, Per Cent	Composition of Vapor, Per Cent HNO_3			
	B. and C.	Babor	B. and S.	Pascal
5.00	0.048	—	—	—
10.00	0.200	—	—	—
12.50	0.35	—	—	—
13.45	—	—	0.46	—
15.00	0.55	—	—	—
17.50	0.75	—	—	—
20.00	1.05	—	—	—
20.58	—	—	1.26	—
22.50	1.45	—	—	—
24.20	—	—	—	2.16
25.00	2.20	—	—	—
27.50	3.00	—	—	—
30.00	4.10	—	—	—
31.75	—	—	4.94	—
32.50	5.60	—	—	—
33.00	—	—	—	5.90
35.00	7.30	—	—	—
37.50	9.40	—	—	—
37.99	—	—	9.20	—
40.00	12.00	—	—	—
42.50	14.90	—	—	—
43.50	—	—	14.86	—
45.00	18.00	—	—	—
47.50	22.20	—	—	—
47.77	—	—	21.71	—
49.80	—	—	—	19.85
50.00	26.50	—	—	—
52.50	31.10	—	—	—
53.96	—	—	33.51	—
55.00	35.50	—	—	—
56.60	—	—	39.37	—
57.50	41.70	—	—	—
60.00	47.80	—	—	50.02
61.47	—	—	51.34	—
62.50	54.60	—	—	—
62.64	—	—	54.46	—
65.00	60.80	—	—	—
65.18	—	—	60.62	—
67.43	—	—	65.97	—
67.50	66.80	—	—	—
67.89	—	—	67.84	—
68.00	(68.00)	—	68.00	—
68.40	—	—	—	68.40
70.00	—	73.22	—	—
70.10	—	—	—	74.00
70.16	—	—	72.56	—
73.26	—	—	79.63	—
74.00	—	82.14	—	—
75.12	—	—	—	91.50
78.00	—	88.89	—	—
78.92	—	—	88.54	—

TABLE II—*Continued.*

Strength of Acid, Per Cent	Composition of Vapor, Per Cent HNO_3			
	B. and C.	Babor	B. and S.	Pascal
79.73	—	—	—	96.70
80.00	—	91.34	—	—
81.52	—	—	92.08	—
82.20	—	—	92.87	—
84.00	—	95.10	—	—
84.36	—	—	95.72	—
84.65	—	—	—	97.45
88.00	—	97.69	—	—
88.66	—	—	97.16	—
89.65	—	—	—	99.41
90.00	—	98.53	—	—
90.02	—	—	97.34	—
90.27	—	—	97.68	—
92.00	—	99.01	—	—
93.93	—	—	98.52	—
95.38	—	—	—	99.63

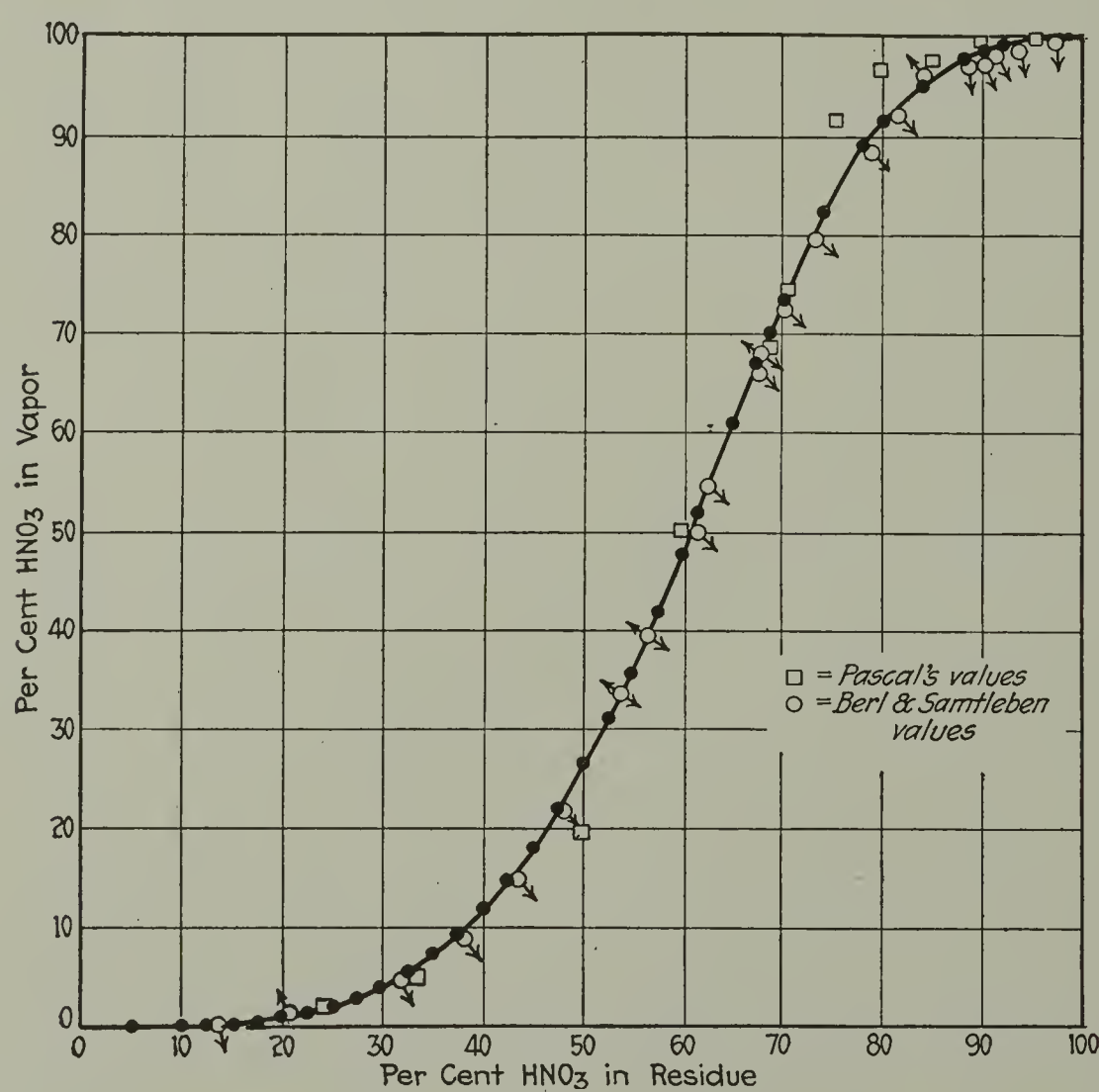


FIG. 3. Equilibrium between Liquid and Vapor in Distilling HNO_3

those of this work. It is quite evident that the results of Pascal are very erratic at the higher temperatures while those of Berl and Samtleben are much more satisfactory. The discrepancies occur as have already been predicted, especially when the concentration of vapor is high.

Part II. System Nitric Acid-Sulphuric Acid-Water

Nitric Acid-Sulphuric Acid-Water: It has already been pointed out and shown that when there is any chance for fractionation large errors result when the concentration of the vapor is high. As will be shown in the following data, the concentrations of the vapors with which the experimental work of this investigation deals are mostly high. It is therefore most important that fractionation be prevented.

TABLE III

COMPLETE DATA ON RUN I

Run 1. Bar. = 759.8 mm.

Composition of the solution in the distilling flask at start:

HNO_3..... 33.856 g. Ratio of $HNO_3 = \frac{HNO_3}{HNO_3 + H_2O} = 5.12$ per cent

H_2SO_4..... 63.805 g.

H_2O.....627.753 g. Ratio of $H_2SO_4 = \frac{H_2SO_4}{H_2SO_4 + H_2O} = 9.64$ per cent

Residue	Fraction, g.	HNO_3 in Fraction, g.	Temperature of Bath, deg. C.	Total Distillate, g.	Total HNO_3 Distilled, g.	Total H_2O Distilled, g.	HNO_3 in Residue, g.	$HNO_3 + H_2O$ in Residue, g.	Composition of Residue	
									Ratio HNO_3, Per Cent	Ratio H_2SO_4, Per Cent
							33.859	661.609	5.12	9.64
1	63.691	0.137	105–107	63.691	0.137	63.553	33.722	597.921	5.64	10.16
2	63.041	0.171	107–108	126.731	0.308	126.424	33.551	534.880	6.27	11.29
3	74.911	0.295	108–110	201.643	0.603	201.040	33.256	459.969	7.23	13.01
4	60.694	0.274	110–111	262.337	0.878	261.459	32.981	399.275	8.26	14.84
5	47.235	0.297	111–113	309.574	1.175	308.397	32.684	352.041	9.28	16.65
6	59.866	0.659	113–117	369.438	1.834	367.604	32.025	292.174	10.96	19.70
7	76.495	1.331	117–120	445.933	3.165	442.768	30.694	215.679	14.23	25.65
8	40.741	1.596	120–122	486.673	4.760	481.913	29.099	174.939	16.63	30.44

A solution of known concentration of acids and water was made up and then distilled as previously described in the work on binary system above. The vapor was condensed and the distillate estimated as described above. Tests were made for sulphate but the distillates were free from this impurity.

In all, 56 runs were made and the results are given in Tables III and IV below. Table III gives the complete values and indicates all calculations for Run 1, while table IV gives the other 55 runs in condensed form.

The residue in the distilling flask, after the first fraction was removed, is designated as Residue 1. The second fraction was then subtracted from Residue 1 giving Residue 2, and so on. The compositions of the residues were calculated as ratio of HNO_3 and ratio of H_2SO_4. By ratio of HNO_3 is meant: ratio of the weight of nitric acid in the residue to the sum of the weights of nitric acid and water in the residue, and by the ratio of H_2SO_4 is meant: the

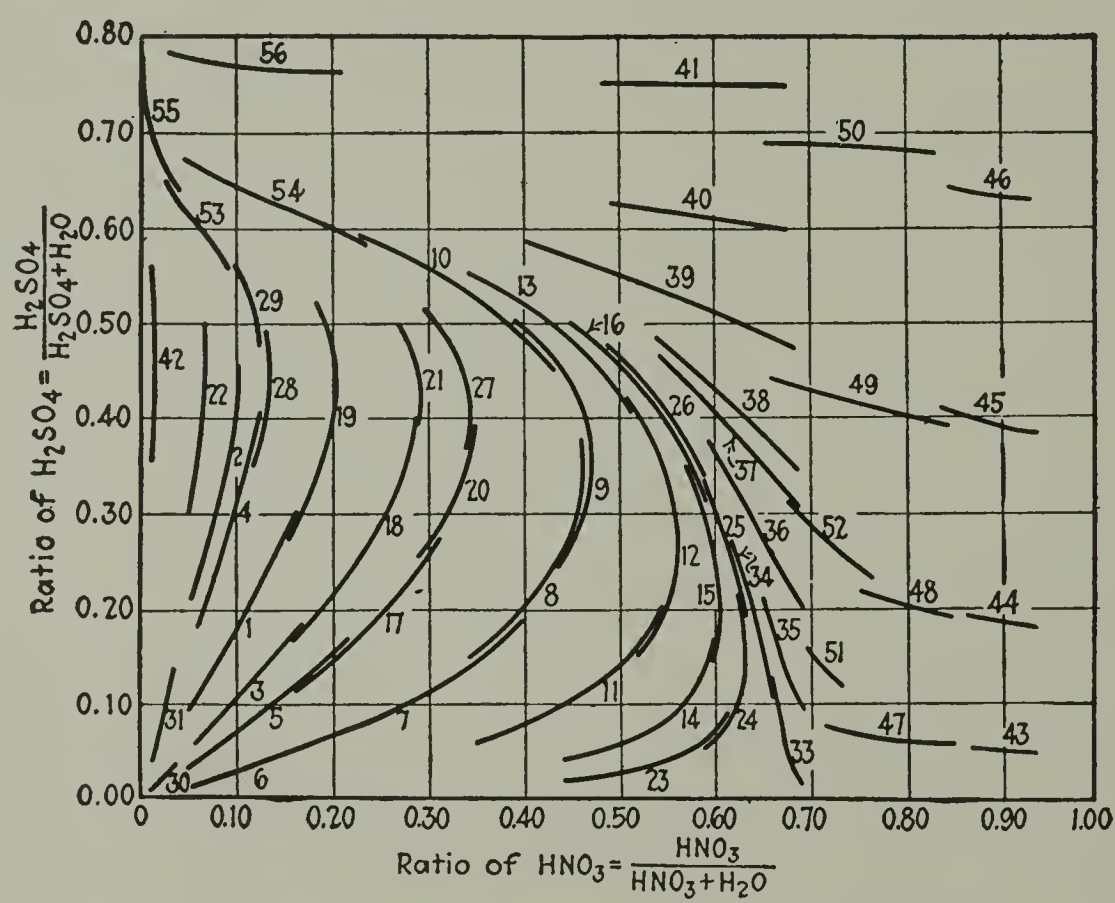


FIG. 4. Distillation of HNO_3 in Presence of H_2SO_4

ratio of the weight of sulphuric acid in the residue to the sum of the weights of sulphuric acid and water in the residue. In other words,

$$\text{Ratio of } HNO_3 = \frac{\text{Weight of } HNO_3 \text{ in the residue}}{\text{Weight of } HNO_3 + \text{weight of } H_2O \text{ in the residue}}$$

$$\text{Ratio of } H_2SO_4 = \frac{\text{Weight of } H_2SO_4 \text{ in the residue}}{\text{Weight of } H_2SO_4 + \text{weight of } H_2O \text{ in the residue}}$$

The compositions of the residues in the 56 runs were plotted as curves 1 to 56 in Fig. 4 with the ratio of HNO_3 as abscissa and the ratio of H_2SO_4 as ordinate. For each run, this gave a curve showing the change in the composition of the residual mixture during distillation as the concentration of the sulphuric acid increased.

The next mixture to be distilled was made up of such composition that the curves would overlap; the second curve having its starting point as nearly as possible on the curve from the previous run, thus minimizing the accumulated error in the last point on a curve. Each complete set of lines shows the change of nitric acid concentration as a single distillation from the starting point until the sulphuric acid reaches nearly 100 per cent concentration.

TABLE IV

SUMMARIZED DATA ON RUNS 2 TO 56

Run 2. Bar. = 760.7 mm.
Composition of Initial Solution
H_2O.....673.382 g.
HNO_3..... 36.066 g.
H_2SO_4.....174.280 g.

Composition of Residues, Ratios of					
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
5.09	20.56	5.13	5.29	5.11	16.04
5.48	22.01	5.68	5.88	5.75	17.88
6.11	24.27	6.48	6.74	6.44	19.91
6.91	27.19	7.44	7.75	7.22	22.15
7.84	30.72	8.81	9.22	8.23	25.09
8.96	35.43	10.23	10.77	9.49	28.93
9.98	41.83	12.84	13.68	11.06	32.21
10.17	46.26	17.22	18.89	12.50	41.08

Run 3. Bar. = 758.3 mm.
Composition of Initial Solution
H_2O.....546.527 g.
HNO_3..... 29.539 g.
H_2SO_4..... 30.548 g.

Run 4. Bar. = 757.8 mm.
Composition of Initial Solution
H_2O.....565.119 g.
HNO_3..... 30.442 g.
H_2SO_4.....107.955 g.

Run 5. Bar. = 766.9 mm.
Composition of Initial Solution
H_2O.....567.550 g.
HNO_3..... 28.605 g.
H_2SO_4..... 19.018 g.

Composition of Residues, Ratios of					
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
4.80	3.24	4.80	1.35	13.59	4.11
5.41	3.67	5.35	1.52	15.25	4.70
6.12	4.18	6.03	1.72	17.12	5.54
6.99	4.80	6.87	1.98	19.56	6.36
8.80	5.59	7.97	2.32	22.48	7.59
9.73	6.81	9.77	2.89	27.06	9.78
11.89	8.46	12.15	3.69	32.96	13.24
16.04	11.78	16.60	5.30	39.81	18.84
21.92	17.10				

Run 6. Bar. = 759.0 mm.
Composition of Initial Solution
H_2O.....578.893 g.
HNO_3..... 29.203 g.
H_2SO_4..... 7.933 g.

Run 7. Bar. = 756.3 mm.
Composition of Initial Solution
H_2O.....491.381 g.
HNO_3..... 77.271 g.
H_2SO_4..... 21.027 g.

Run 8. Bar. = 755.5 mm.
Composition of Initial Solution

H_2O.....384.070 g.
HNO_3.....197.935 g.
H_2SO_4..... 65.581 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
34.01	14.58
36.50	16.52
39.10	18.94
41.69	22.04
44.04	25.85
45.92	31.25
46.02	38.42

Run 9. Bar. = 758.0 mm.
Composition of Initial Solution

H_2O.....351.349 g.
HNO_3.....273.335 g.
H_2SO_4.....111.910 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
43.75	24.16
44.99	26.45
46.10	29.56
46.75	33.43
46.52	37.55
45.05	42.17
43.06	45.49
40.51	48.52
37.45	51.22

Run 10. Bar. = 762.0 mm.
Composition of Initial Solution

H_2O.....311.567 g.
HNO_3.....196.675 g.
H_2SO_4.....306.580 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
38.70	49.60
36.97	51.20
34.64	52.96
31.37	55.03
27.67	57.01
22.52	59.39

Run 11. Bar. = 762.7 mm.
Composition of Initial Solution

H_2O.....393.319 g.
HNO_3.....203.705 g.
H_2SO_4..... 23.515 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
34.12	5.64
36.24	6.28
39.59	7.44
43.07	8.92
46.96	11.10
50.47	13.90
53.24	17.32
55.03	21.14

Run 12. Bar. = 759.4 mm.
Composition of Initial Solution

H_2O.....249.443 g.
HNO_3.....267.390 g.
H_2SO_4..... 43.988 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
51.74	14.99
53.25	17.07
54.63	19.80
55.50	22.82
55.89	26.61
55.42	31.41
53.13	38.09
50.89	41.91

Run 13. Bar. = 763.7 mm.
Composition of Initial Solution

H_2O.....250.512 g.
HNO_3.....262.340 g.
H_2SO_4.....174.093 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
51.15	41.00
50.12	42.63
48.39	44.89
46.19	47.25
43.39	49.72
39.15	52.68
33.88	55.57

Run 14. Bar. = 766.0 mm.

Composition of Initial Solution

H_2O.....335.360 g.
HNO_3.....264.175 g.
H_2SO_4..... 13.777 g.

Run 15. Bar. = 760.0 mm.

Composition of Initial Solution

H_2O.....195.412 g.
HNO_3.....290.415 g.
H_2SO_4..... 32.224 g.

Run 16. Bar. = 764.9 mm.

Composition of Initial Solution

H_2O.....168.185 g.
HNO_3.....246.895 g.
H_2SO_4..... 73.929 g.

Composition of Residues, Ratios of		Composition of Residues, Ratios of		Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
44.06	3.95	59.78	14.16	59.48	30.53
46.45	4.51	59.79	14.18	58.51	33.06
49.69	5.47	60.32	15.87	56.98	36.26
52.62	6.67	60.61	17.60	54.60	40.21
55.37	8.29	60.74	20.27	51.15	44.65
58.07	11.05	60.54	23.51	42.96	51.54
59.78	14.64	59.58	28.05		
60.35	20.06	56.86	35.31		

Run 17. Bar. = 766.6 mm.

Composition of Initial Solution

H_2O.....414.155 g.
HNO_3..... 76.823 g.
H_2SO_4..... 51.319 g.

Run 18. Bar. = 755.3 mm.

Composition of Initial Solution

H_2O.....407.884 g.
HNO_3..... 75.425 g.
H_2SO_4..... 78.979 g.

Run 19. Bar. = 764.0 mm

Composition of Initial Solution

H_2O.....398.807 g.
HNO_3..... 73.113 g.
H_2SO_4.....153.580 g.

Composition of Residues, Ratios of		Composition of Residues, Ratios of		Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
15.65	11.03	15.60	16.22	15.49	27.80
17.20	12.29	17.08	17.95	16.69	30.45
19.39	14.16	18.95	20.26	17.89	33.46
22.38	16.91	21.21	23.25	19.26	37.73
26.17	20.88	23.55	26.73	20.10	42.33
31.22	27.60	26.03	31.22	19.90	46.84
		28.09	36.69	18.04	52.04
		28.78	42.87		

Run 20. Bar. = 767.0 mm.
Composition of Initial Solution

H_2O.....349.192 g.
HNO_3.....142.475 g.
H_2SO_4.....118.582 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
28.98	25.35
30.53	27.68
32.16	30.64
33.80	34.92
34.53	39.38

Run 21. Bar. = 757.5 mm.
Composition of Initial Solution

H_2O.....339.817 g.
HNO_3.....136.782 g.
H_2SO_4.....217.220 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
28.70	39.00
28.98	42.11
28.42	45.98
26.86	49.76

Run 22. Bar. = 762.0 mm
Composition of Initial Solution

H_2O.....429.146 g.
HNO_3..... 21.255 g.
H_2SO_4.....181.122 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
4.72	29.68
5.16	32.16
5.62	35.02
6.10	38.35
6.48	41.99
6.69	46.70
6.43	50.45

Run 23. Bar. = 760.7 mm.
Composition of Initial Solution

H_2O.....302.092 g.
HNO_3.....238.150 g.
H_2SO_4..... 5.963 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
44.08	1.94
46.87	2.26
49.36	2.62
52.23	3.15
55.30	3.95
58.51	5.34
60.70	7.10
62.01	9.24

Run 24. Bar. = 770.5 mm.
Composition of Initial Solution

H_2O.....187.655 g.
HNO_3.....265.930 g.
H_2SO_4..... 10.433 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
58.63	5.27
59.82	6.01
60.97	7.04
62.01	8.48
62.80	10.48
63.26	13.29
63.21	18.29

Run 25. Bar. = 758.1 mm.
Composition of Initial Solution

H_2O.....171.183 g.
HNO_3.....294.460 g.
H_2SO_4..... 30.172 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
63.24	14.98
63.21	16.81
63.06	18.67
62.65	21.36
61.94	24.66
60.71	28.85
58.85	33.49

Run 26. Bar. = 758.5 mm.
Composition of Initial Solution

H_2O.....239.371 g.
HNO_3.....342.949 g.
H_2SO_4.....122.180 g.

Run 27. Bar. = 772.6 mm.
Composition of Initial Solution

H_2O.....286.096 g.
HNO_3.....146.038 g.
H_2SO_4.....159.295 g.

Run 28. Bar. = 768.1 mm.
Composition of Initial Solution

H_2O.....343.712 g.
HNO_3..... 46.019 g.
H_2SO_4.....191.210 g.

Composition of Residues, Ratios of		Composition of Residues, Ratios of		Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
58.89	33.79	33.79	35.76	11.81	35.75
57.89	35.80	34.36	38.80	12.50	38.59
56.74	37.84	34.16	43.10	13.01	41.51
54.90	40.63	32.76	47.09	13.29	45.04
52.50	43.72	29.17	51.81	12.87	49.32
48.46	47.76				

Run 29. Bar. = 760.8 mm.
Composition of Initial Solution

H_2O.....359.592 g.
HNO_3..... 50.481 g.
H_2SO_4.....326.780 g.

Run 30. Bar. = 761.0 mm.
Composition of Initial Solution

H_2O.....504.795 g.
HNO_3..... 4.909 g.
H_2SO_4..... 5.068 g.

Run 31. Bar. = 768.0 mm
Composition of Initial Solution

H_2O.....496.884 g.
HNO_3..... 4.824 g.
H_2SO_4..... 18.742 g.

Composition of Residues, Ratios of		Composition of Residues, Ratios of		Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
12.31	47.61	0.96	0.99	0.96	3.64
11.75	50.80	1.05	1.81	1.12	4.25
10.54	54.00	1.17	1.22	1.26	4.84
9.11	56.50	1.31	1.37	1.46	5.65
		1.51	1.58	1.76	6.92
		1.78	1.87	2.18	8.69
		2.19	2.31	2.94	11.81
		2.83	3.03	3.52	14.14

Run 32. Bar. = 774.0 mm.
Composition of Initial Solution

H_2O.....180.018 g.
HNO_3.....401.000 g.
H_2SO_4..... 3.327 g.

Run 33. Bar. = 759.5 mm.
Composition of Initial Solution

H_2O.....200.460 g.
HNO_3.....423.450 g.
H_2SO_4..... 8.178 g.

Run 34. Bar. = 762.3 mm.
Composition of Initial Solution

H_2O.....213.697 g.
HNO_3.....411.160 g.
H_2SO_4..... 29.515 g.

Composition of Residues, Ratios of		Composition of Residues, Ratios of		Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
69.02	1.82	67.87	3.92	65.80	12.14
68.88	1.95	67.76	4.32	65.54	13.46
68.72	2.14	67.63	4.78	65.16	15.21
68.55	2.37	67.45	5.56	64.65	17.23
68.37	2.70	67.20	6.71	63.92	19.92
68.14	3.19	66.89	8.11	62.76	23.81
67.84	4.03	66.39	10.40	61.42	27.48
67.50	5.09	65.80	13.01		

Run 35. Bar. = 769.0 mm.
Composition of Initial Solution

H_2O.....119.149 g.
HNO_3.....271.630 g.
H_2SO_4..... 12.074 g.

Run 36. Bar. = 750.7 mm.
Composition of Initial Solution

H_2O.....147.028 g.
HNO_3.....332.385 g.
H_2SO_4..... 36.911 g.

Run 37. Bar. = 757.0 mm.
Composition of Initial Solution

H_2O.....156.897 g.
HNO_3.....351.050 g.
H_2SO_4..... 67.896 g.

Composition of Residues, Ratios of		Composition of Residues, Ratios of		Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
69.51	9.20	69.33	20.07	69.11	30.20
68.93	10.10	68.32	21.54	67.64	31.82
68.35	11.24	67.31	23.31	65.84	33.89
67.54	13.19	66.04	25.64	63.81	36.27
66.49	16.32	64.24	28.99	61.53	38.97
64.68	21.65	62.02	33.10	57.95	42.89
		59.20	37.71	53.92	46.68

Run 38. Bar. = 765.4 mm.
Composition of Initial Solution

H_2O.....161.291 g.
HNO_3.....359.030 g.
H_2SO_4..... 84.053 g.

Run 39. Bar. = 758.2 mm.
Composition of Initial Solution

H_2O.....167.929 g.
HNO_3.....365.540 g.
H_2SO_4.....151.880 g.

Run 40. Bar. = 757.7 mm.
Composition of Initial Solution

H_2O.....139.137 g.
HNO_3.....292.290 g.
H_2SO_4.....208.410 g.

Composition of Residues, Ratios of		Composition of Residues, Ratios of		Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
69.00	34.26	68.52	47.49	67.75	59.97
67.59	35.53	66.68	48.24	64.91	60.38
66.22	36.97	64.37	49.23	60.91	60.99
64.31	38.84	61.18	50.57	56.33	61.69
61.42	41.71	57.68	52.07	50.89	62.54
57.90	45.01	53.66	53.71	48.80	62.85
53.50	48.56	47.02	56.19		
		40.31	58.41		

Run 41. Bar. = 766.5 mm.
Composition of Initial Solution

H_2O.....129.263 g.
HNO_3.....270.140 g.
H_2SO_4.....384.300 g.

Run 42. Bar. = 764.5 mm.
Composition of Initial Solution

H_2O.....348.910 g.
HNO_3..... 3.360 g.
H_2SO_4.....188.080 g.

Run 43. Bar. = 762.0 mm.
Composition of Initial Solution

H_2O..... 20.107 g.
HNO_3.....316.020 g.
H_2SO_4..... 1.064 g.

Composition of Residues, Ratios of		Composition of Residues, Ratios of		Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
67.64	74.83	0.95	35.02	94.06	5.05
64.55	74.93	1.06	38.61	93.21	5.06
59.57	75.07	1.14	42.13	92.27	5.14
55.33	75.19	1.20	46.37	90.97	5.23
50.05	75.33	1.17	50.38	89.13	5.35
48.02	75.39	1.04	54.42	86.33	5.59
		0.92	56.47		

Run 44. Bar. = 762. mm.
Composition of Initial Solution

H_2O..... 29.755 g.
HNO_3.....466.960 g.
H_2SO_4..... 6.685 g.

Run 45. Bar. = 762.1 mm.
Composition of Initial Solution

H_2O..... 17.090 g.
HNO_3.....262.000 g.
H_2SO_4..... 10.887 g.

Run 46. Bar. = 758.5 mm.
Composition of Initial Solution

H_2O..... 21.406 g.
HNO_3.....307.045 g.
H_2SO_4..... 37.236 g.

Composition of Residues, Ratios of		Composition of Residues, Ratios of		Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
94.01	18.34	93.88	38.91	93.48	63.50
93.53	18.32	93.01	38.69	92.46	63.45
92.95	18.36	91.89	38.90	91.22	63.46
92.18	18.47	90.34	39.40	89.94	63.70
91.36	18.58	87.57	40.10	87.74	64.07
90.18	18.78	83.22	41.37	84.64	64.55
88.82	19.10				
86.03	19.77				

Run 47. Bar. = 754.4 mm.
Composition of Initial Solution

H_2O..... 53.634 g.
HNO_3.....306.720 g.
H_2SO_4..... 3.398 g.

Run 48. Bar. = 756.0 mm.
Composition of Initial Solution

H_2O..... 52.093 g.
HNO_3.....295.070 g.
H_2SO_4..... 12.526 g.

Run 49. Bar. = 754.3 mm.
Composition of Initial Solution

H_2O..... 49.621 g.
HNO_3.....274.580 g.
H_2SO_4..... 32.167 g.

Composition of Residues, Ratios of		Composition of Residues, Ratios of		Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
85.12	5.96	85.00	19.39	84.70	39.33
83.56	6.09	83.54	19.72	82.62	39.85
81.39	6.28	81.01	20.28	80.16	40.43
78.68	6.55	77.17	21.12	77.25	41.22
75.40	6.99	75.00	22.15	73.46	42.16
71.13	7.89			69.46	43.21
				65.57	44.33

Run 50. Bar. = 756.0 mm.
Composition of Initial Solution

H_2O..... 36.193 g.
HNO_3.....183.250 g.
H_2SO_4..... 76.520 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
83.51	67.89
80.80	68.14
77.56	68.38
72.10	68.67
65.10	68.94

Run 51. Bar. = 759.0 mm.
Composition of Initial Solution

H_2O..... 86.935 g.
HNO_3.....246.825 g.
H_2SO_4..... 11.330 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
73.95	11.53
72.96	12.35
71.61	13.58
70.41	15.03
69.38	16.56

Run 52. Bar. = 750.4 mm.
Composition of Initial Solution

H_2O..... 61.971 g.
HNO_3.....204.560 g.
H_2SO_4..... 18.923 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
76.75	23.39
75.01	24.50
72.98	26.27
70.74	28.36
67.62	31.51

Run 53. Bar. = 758.1 mm.
Composition of Initial Solution

H_2O.....105.033 g.
HNO_3..... 10.742 g.
H_2SO_4.....131.980 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
9.28	55.68
7.20	58.77
5.34	61.19
3.87	63.08
3.24	63.94
2.68	65.20

Run 54. Bar. = 759.6 mm.
Composition of Initial Solution

H_2O.....189.755 g.
HNO_3..... 57.750 g.
H_2SO_4.....265.170 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
23.33	58.29
19.31	60.11
14.43	62.19
10.12	64.07
6.21	66.04
4.06	67.49

Run 55. Bar. = 769.4 mm.
Composition of Initial Solution

H_2O.....230.613 g.
HNO_3..... 10.337 g.
H_2SO_4.....396.830 g.

Composition of Residues, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent
4.29	63.25
2.92	65.52
1.69	68.06
0.94	70.25
0.30	73.29
0.11	76.13
0.06	78.61

Run 56. Bar. = 764.0 mm.
Composition of Initial Solution

H_2O.....142.990 g.
HNO_3..... 38.284 g.
H_2SO_4.....457.510 g.

Composition of Residues, Ratios of

HNO_3 Per Cent	H_2SO_4 Per Cent
21.12	76.19
14.57	76.55
8.78	77.12
2.57	78.29

Next fraction contained H_2SO_4

In the Tables III and IV the composition of the residues includes the nitrous acid reported as nitric acid. Table V gives the per cent of N_2O_3 in the fractions containing oxides of nitrogen, due to decomposition of the HNO_3 in the boiling liquid.

TABLE V

FRACTIONS CONTAINING OXIDES OF NITROGEN

Run 41		Run 43		Run 44		Run 45	
Fraction	% N_2O_3	Fraction	% N_2O_3	Fraction	% N_2O_3	Fraction	% N_2O_3
1	0.40	1	0.14	1	0.10	1	0.26
2	0.21	2	0.19	2	0.06	2	0.19
3	0.08	3	0.08	3	0.02	3	0.09
4	<0.01	4	0.02	4	<0.01	4	0.05
		5	<0.01			5	0.02

Run 46		Run 47		Run 48		Run 49	
Fraction	% N_2O_3	Fraction	%N_2O_3	Fraction	% N_2O_3	Fraction	% N_2O_3
1	1.02	1	0.17	1	0.24	1	0.34
2	0.63	2	0.05	2	0.12	2	0.21
3	0.38	3	0.02	3	0.04	3	0.14
4	0.27	4	<0.01	4	0.01	4	0.09
5	0.13					5	<0.01

Run 50		Run 51		Run 52	
Fraction	% N_2O_3	Fraction	% N_2O_3	Fraction	% N_2O_3
1	0.40	1	0.02	1	0.09
2	0.28	2	<0.01	2	0.04
3	0.15			3	0.01
4	0.03				

In Runs 44, 45 and 46 the first fraction contained oxides of nitrogen due to decompositions and gave a vapor which titrated slightly above 100 per cent nitric acid.

The curves were plotted on a large scale and then using these as a guide smooth continuous curves were drawn representing continuous distillations. These curves are given in Fig. 5. Values were then read from these curves and given in Table VI.

TABLE VI

Distillation Data from Curves in Fig. 5

Curve 1, Ratios of		Curve 2, Ratios of		Curve 3, Ratios of		Curve 4, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.31	5.00	0.91	5.00	1.76	5.00	1.45	2.50
0.54	10.00	1.80	10.00	3.50	10.00	2.88	5.00
0.69	15.00	2.65	15.00	5.26	15.00	5.74	10.00
0.80	20.00	3.46	20.00	6.93	20.00	8.59	15.00
0.90	25.00	4.29	25.00	8.50	25.00	11.30	20.00
0.99	30.00	5.05	30.00	9.90	30.00	13.97	25.00
1.07	35.00	5.75	35.00	11.30	35.00	16.40	30.00
1.14	40.00	6.30	40.00	11.75	37.50	18.41	35.00
1.19	45.00	6.52	42.50	12.20	40.00	19.22	37.50
1.19	45.19	6.73	45.00	12.52	42.50	19.79	40.00
1.10	50.00	6.66	47.50	12.60	44.51	20.10	42.50
0.93	55.00	6.41	50.00	12.59	45.00	20.16	43.12
0.69	60.00	5.54	55.00	12.38	47.50	20.05	45.00
0.40	65.00	3.89	60.00	11.98	50.00	19.73	47.50
0.25	70.00	2.00	65.00	11.15	52.50	19.00	50.00
		0.51	70.00	9.98	55.00	15.55	55.00
				8.33	57.50	12.57	57.50
				6.40	60.00	9.02	60.00
				4.50	62.50	6.21	62.50
				2.87	65.00	4.00	65.00
				1.70	67.50	2.30	67.50
				0.90	70.00	1.23	70.00
				0.20	75.00		

Curve 5, Ratios of		Curve 6, Ratios of		Curve 7, Ratios of		Curve 8, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.39	2.50	3.85	2.50	5.00	1.36	5.45	0.55
4.73	5.00	7.42	5.00	8.72	2.50	10.15	1.08
9.39	10.00	14.18	10.00	10.00	2.93	15.00	1.70
13.70	15.00	20.08	15.00	16.00	5.00	20.00	2.42
17.69	20.00	25.00	20.00	22.00	7.50	25.00	3.32
21.30	25.00	29.07	25.00	27.00	10.00	30.00	4.43
24.34	30.00	32.20	30.00	30.00	11.60	32.19	5.00
25.51	32.50	34.10	35.00	35.09	15.00	35.00	5.82
26.45	35.00	34.55	37.50	40.62	20.00	39.95	7.50
27.08	37.50	34.70	38.87	44.09	25.00	45.18	10.00
27.40	40.00	34.60	40.00	46.10	30.00	51.60	15.00
27.49	41.34	33.85	45.00	46.72	32.84	54.73	20.00
27.45	42.50	31.00	50.00	46.60	35.00	55.53	22.50
27.10	45.00	28.71	52.50	45.41	40.00	55.90	25.00
25.06	50.00	25.39	55.00	43.10	45.00	55.98	25.06
20.65	55.00	20.98	57.50	38.80	50.00	55.35	30.00
17.17	57.50	15.70	60.00	35.65	52.50	53.82	35.00
12.60	60.00	10.59	62.50	31.60	55.00	51.42	40.00
8.15	62.50	6.58	65.00	21.00	60.00	47.78	45.00
5.00	65.00	3.88	67.50	9.18	65.00	42.80	50.00
2.91	67.50	2.10	70.00	2.60	70.00	35.20	55.00
1.65	70.00					23.25	60.00
0.89	72.50						
0.60	75.00						
0.31	80.00						
0.20	85.00						
0.10	90.00						
0.08	95.00						

TABLE VI (*continued*)

Curve 9, Ratios of		Curve 10, Ratios of		Curve 11, Ratios of		Curve 12, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
0.00	0.00	0.00	0.00	95.00	0.10	95.00	5.02
5.00	0.20	5.00	0.12	90.00	0.13	90.00	5.32
10.00	0.45	9.80	0.25	85.00	0.19	85.00	5.65
15.00	0.70	14.60	0.40	80.00	0.28	80.00	6.05
20.00	1.05	20.00	0.60	75.00	0.38	75.00	6.78
25.00	1.40	25.00	0.84	70.00	1.10	72.96	7.50
30.00	1.88	30.00	1.11	68.45	2.50	70.00	9.41
35.00	2.40	35.00	1.44	67.40	5.00	69.45	10.00
40.00	3.07	40.00	1.82	66.90	7.50	67.90	12.50
45.00	4.05	44.60	2.21	66.40	10.00	66.95	15.00
50.00	5.58	50.00	2.75	65.25	15.00	65.35	20.00
54.13	7.50	55.00	3.95	63.89	20.00	65.00	21.00
57.20	10.00	57.65	5.00	62.35	25.00	63.40	25.00
58.95	12.50	61.04	7.50	60.58	30.00	61.19	30.00
60.00	15.15	62.35	10.00			58.60	35.00
60.43	17.50	63.00	13.10			55.50	40.00
60.71	20.28	63.17	15.00				
60.15	25.00	63.19	16.68				
58.89	30.00	63.00	18.92				
56.79	35.00	62.90	20.00				
53.90	40.00	61.90	25.00				
49.98	45.00	60.30	30.00				
44.60	50.00	58.15	35.00				
		55.20	40.00				
		51.10	45.00				
		45.30	50.00				

Curve 13, Ratios of		Curve 14, Ratios of		Curve 15, Ratios of		Curve 16, Ratios of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
95.00	18.02	95.00	38.20	95.00	58.09	95.00	74.50
92.00	18.25	90.00	38.81	90.00	58.20	90.00	74.55
90.00	18.57	85.00	39.89	85.00	58.40	85.00	74.60
85.00	19.80	80.00	41.30	80.00	58.73	80.00	74.63
80.00	21.61	75.00	43.14	75.00	59.14	75.00	74.70
75.00	24.57	70.00	45.15	70.00	59.65	70.00	74.85
70.00	29.12	65.00	47.25	65.00	60.34	65.00	74.94
65.00	34.70	60.00	49.48	60.00	61.18	60.00	75.10
60.00	40.45	55.00	51.68	55.00	61.90	55.00	75.15
55.00	45.40	50.00	53.80	50.00	62.65	50.00	75.26
50.00	49.32	45.00	55.73	45.00	63.41	45.00	75.40
49.00	50.00	40.00	57.63	40.00	64.21	40.00	75.53
45.00	52.45	35.00	59.27	35.00	64.98	35.00	75.68
40.00	55.00	30.00	60.70	28.53	65.81	30.00	75.80
35.00	57.18	25.00	62.10	23.35	66.67	25.00	76.00
30.00	59.00	18.44	63.41	17.80	67.59	20.00	76.20
				11.90	68.71	15.00	76.50
				6.00	70.18	10.00	76.90
				5.00	70.60	7.50	77.30
						3.50	78.00

Application and Discussion of Results

Determination of the Vapor Phase

The composition of the vapor phase was obtained in the following manner: Sections of the curves in Fig. 5 were plotted on a large scale, as shown in Fig. 6. The curve used as an illustration is a portion of curve 13 from Fig. 5. The problem is to find the

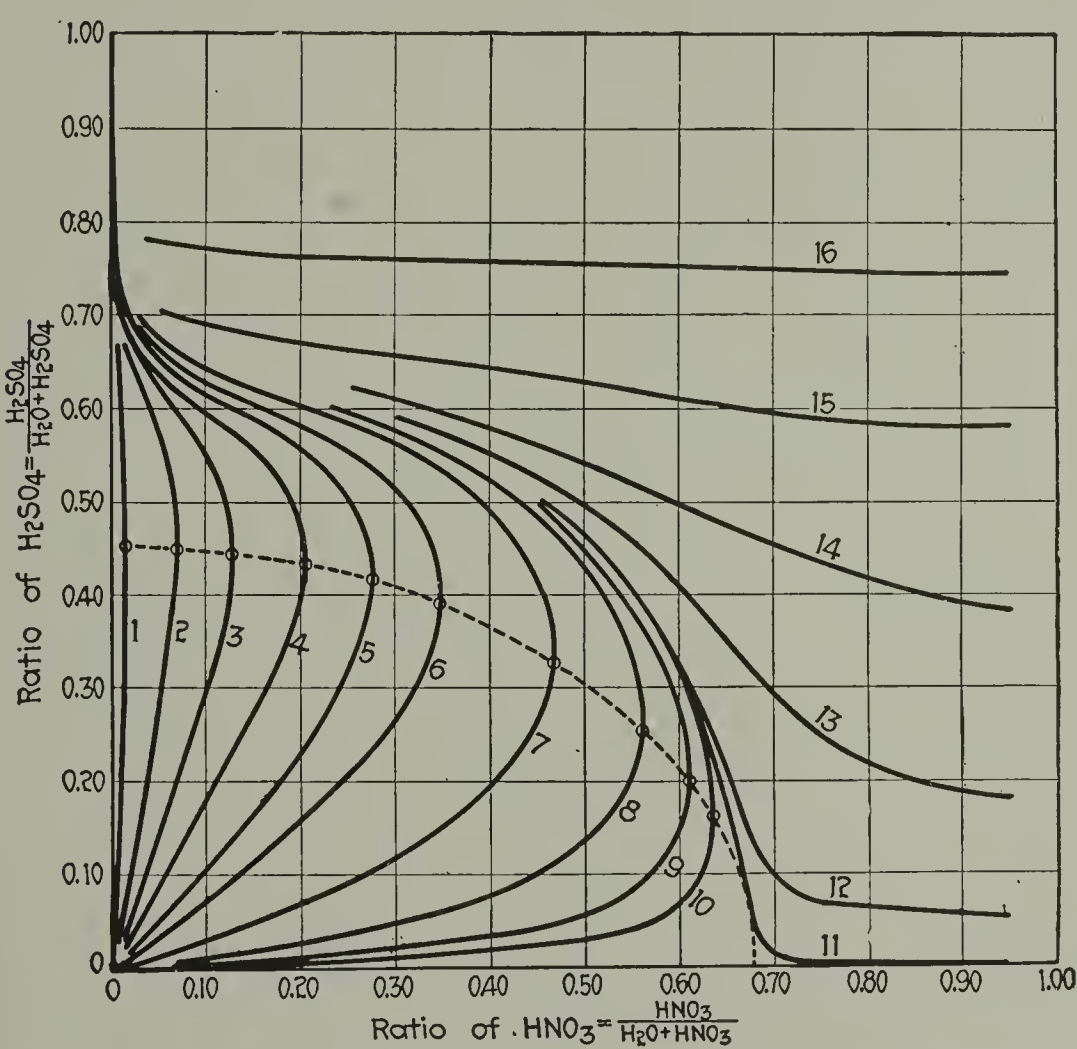


Fig. 5. Distillation Curves Derived from Those in Fig. 4

composition of the vapor in equilibrium with a boiling solution whose composition is represented by point *A* in the figure. The composition of this solution is:

$$\text{Ratio of } HNO_3 = 74.40 \text{ per cent}$$

$$\text{Ratio of } H_2SO_4 = 25.00 \text{ per cent}$$

Two points on either side of *A* are chosen as *B* and *C*. From the plot the compositions of the liquids at *B* and *C* are

B, Ratio of		*C*, Ratio of	
HNO_3 Per Cent	H_2SO_4 Per Cent	HNO_3 Per Cent	H_2SO_4 Per Cent
75.80	24.00	73.21	26.00

Since the sulphuric acid does not distill over, the amount of H_2SO_4 in the residues along each curve is constant for that curve. Hence the amount of H_2SO_4 in the residues at *B* and *C* is the same. Assume this to be 100 g. Then since the ratio of

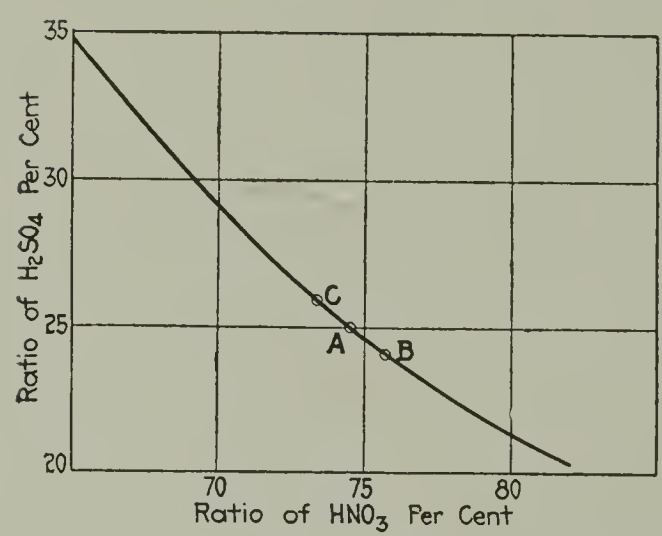


FIG. 6. Calculating Vapor Composition

$$H_2SO_4 = \frac{H_2SO_4}{H_2SO_4 + H_2O},$$

and if the amount of water is represented by x, we have for point *B*

$$\frac{100}{100 + x} = 0.24$$

and for point *C*

$$\frac{100}{100 + x} = 0.26$$

Solving for x,

H_2O content at B = 316.68 g.
H_2O content at C = 284.59 g.

In the expression for the ratio of HNO_3, $HNO_3/(HNO_3 + H_2O)$, let y represent the amount of HNO_3, then for point *B*

$$\frac{y}{y + 316.68} = 0.7580$$

and for point *C*

$$\frac{y}{y + 284.59} = 0.7321$$

Solving for y,

HNO_3 content at B = 991.92 g.
HNO_3 content at C = 777.72 g.

Thus the compositions of the residues at points *B* and *C* are as follows:

	B, g.	*C*, g.	Difference, g.
H_2SO_4	100.00	100.00	0.0
HNO_3	991.92	777.72	214.20
H_2O	316.68	284.59	32.09

The difference is the distillate and its composition is taken as that of the vapor in equilibrium with a boiling solution of composition *A*.

The above procedure was followed in calculating the vapor phase for all points on the curves which have a ratio of H_2SO_4 equal to a multiple of 5 per cent. The values are given in Table

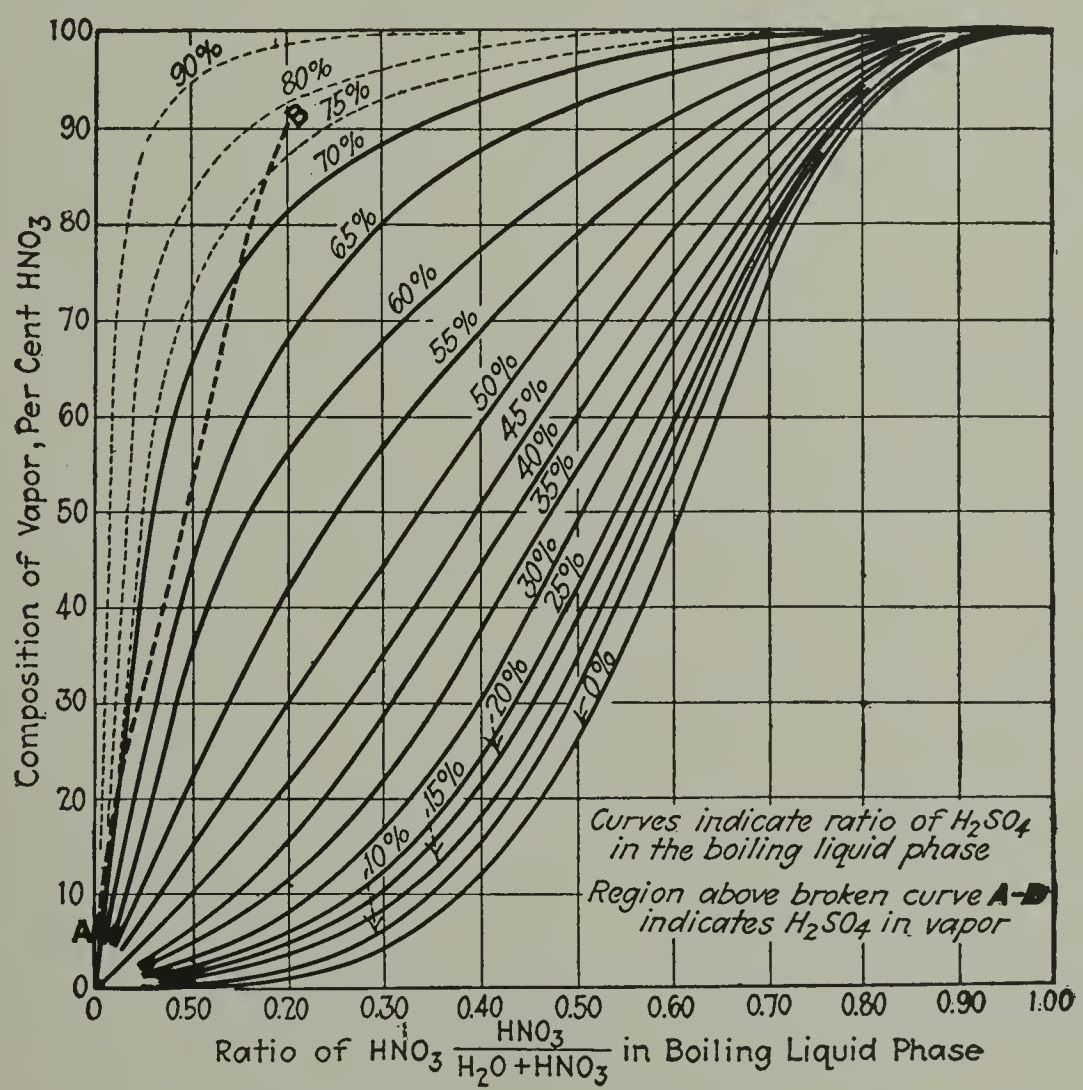


FIG. 7. Liquid-Vapor Equilibrium in Presence of H_2SO_4

VII. The values obtained by Berl and Samtleben were recalculated on the ratio basis and extrapolated to the nearest curves. Some of their values are also given in Table VII for comparison.

TABLE VII

VAPOR IN EQUILIBRIUM WITH BOILING AQUEOUS MIXTURE OF HNO_3 IN THE PRESENCE OF VARIOUS RATIOS OF H_2SO_4

Ratio of H_2SO_4, Per Cent	Ratio of HNO_3, Per Cent	Composition of Vapor, Per Cent HNO_3	
		B. and C.	B. and S.
10	0.54	0.05	
	1.80	0.10	
	3.50	0.20	
	5.74	0.54	
	9.39	0.65	
	14.18	1.16	
	27.00	4.40	
	45.18	23.02	
	57.20	47.11	
	62.35	58.39	
	63.00		60.80 L
	66.40	68.31	
	69.45	75.20	
15	0.69	0.33	
	2.65	0.43	
	5.26	0.66	
	8.59	0.92	
	13.70	1.53	
	18.64		3.02
	20.08	3.19	
	33.10		12.32
	35.09	12.42	
	51.60	36.95	
	59.95	55.71	
	63.17	62.01	
	64.00		63.80 L
	65.25	67.13	
	66.95	72.10	
20	0.86	0.40	
	3.46	0.74	
	6.93	1.23	
	11.30	1.86	
	17.69	3.69	
	24.00		4.50 L
	25.00	7.01	
	39.20		20.30
	40.62	21.96	
	52.00		42.30
	54.73	47.39	
	60.69	60.09	
	62.68	64.78	
	63.40		65.90
	63.89	67.40	
	65.35	70.62	
	84.28	96.71	

TABLE VII—(*Continued*)

Ratio of H_2SO_4, Per Cent	Ratio of HNO_3, Per Cent	Composition of Vapor, Per Cent HNO_3	
		B. and C.	B. and S.
25	0.90	0.43	
	4.29	1.14	
	8.50	2.21	
	13.97	3.54	
	17.30		5.21
	21.30	6.10	
	28.00		9.50 L
	29.07	10.86	
	43.20		29.40
	44.09	30.85	
	52.90		47.20 L
	55.90	53.50	
	60.15	62.72	
	61.90	66.04	
	62.35	66.41	
	63.40	69.77	
	74.40	86.98	
30	0.99	0.62	
	5.05	1.58	
	9.90	3.25	
	16.40	5.51	
	21.20		9.80
	24.34	11.27	
	30.60		18.70
	32.20	19.61	
	46.10	40.80	
	53.40		50.20 L
	55.35	58.77	
	58.89	64.92	
	60.30	67.16	
	61.19	69.01	
	69.20	81.98	
35	1.07	0.72	
	5.75	2.71	
	11.30	5.74	
	18.41	10.01	
	23.10		12.30 L
	26.45	17.56	
	33.10		23.90 L
	34.10	27.82	
	46.60	48.97	
	52.20		56.20 L
	53.82	61.29	
	56.79	65.87	
	58.15	67.67	
	64.75	77.35	

TABLE VII—(*Continued*)

Ratio of H_2SO_4, Per Cent	Ratio of HNO_3, Per Cent	Composition of Vapor, Per Cent HNO_3	
		B. and C.	B. and S.
40	1.14	0.84	
	6.30	3.80	
	12.20	8.06	
	19.79	15.35	
	24.20		21.10
	27.40	24.86	
	32.10		32.00
	34.60	35.81	
	35.40		36.60
	41.40		44.20 L
	45.41	52.74	
	51.42	62.12	
	53.90	65.96	
	55.20	67.82	
	60.43	74.33	
	66.30		82.60
	84.55	98.13	
45	1.19	1.19	
	6.73	6.73	
	12.59	12.80	
	20.05	21.27	
	27.10	31.18	
	31.20		39.80
	33.85	41.08	
	34.00		38.30 L
	43.10	54.73	
	47.78	62.32	
	49.98	65.29	
	51.10	67.12	
	55.42	72.80	
	59.20		78.80
	70.33	90.17	
50	1.10	1.74	
	6.41	9.82	
	11.98	17.38	
	19.00	28.15	
	21.80		27.20 L
	25.06	37.10	
	31.00	46.29	
	38.80	57.52	
	42.80	62.66	
	49.00	70.78	
	58.90	82.41	
55	0.93	1.90	
	5.54	12.01	
	9.98	21.39	
	15.55	33.83	

TABLE VII—(*Continued*)

Ratio of H_2SO_4, Per Cent	Ratio of HNO_3, Per Cent	Composition of Vapor, Per Cent HNO_3	
		B. and C.	B. and S.
55	20.65	42.73	
	24.20		43.8 L
	25.39	50.73	
	27.00		47.20 L
	31.60	58.91	
	35.20	63.00	
	40.00	68.47	
	46.98	75.91	
60	0.69	1.93	
	3.89	11.62	
	6.40	21.89	
	9.02	32.35	
	11.10		35.20 L
	12.60	43.03	
	14.30		45.00 L
	15.70	49.50	
	16.80		48.80 L
	21.00	57.46	
	26.50		62.30 L
	32.50	69.88	
	67.35	94.96	
65	0.40	1.47	
	2.87	14.44	
	4.00	19.55	
	5.00	23.96	
	6.58	30.70	
	8.30		41.90
	9.18	42.02	
	10.91		58.20
	34.78	84.30	
	60.20		93.80 L
70	0.90	5.93	
	1.65	8.87	
	2.81		52.6*
	3.01		34.4
	10.70	58.0*	
75	0.60	2.26	
	63.25	98.69	
80	0.31	1.02	
	2.27	26.00	
	7.30		78.1*
85	0.20	0.33	

* Vapor contained H_2SO_4.

The results in Tables II and VII are shown in Fig. 7. The region above the broken line *A–B* represents those solutions which have an appreciable vapor pressure of H_2SO_4 at the boiling point under normal atmospheric pressure. Figure 8 is a photograph of a solid diagram wherein the composition of the liquid phase, plotted

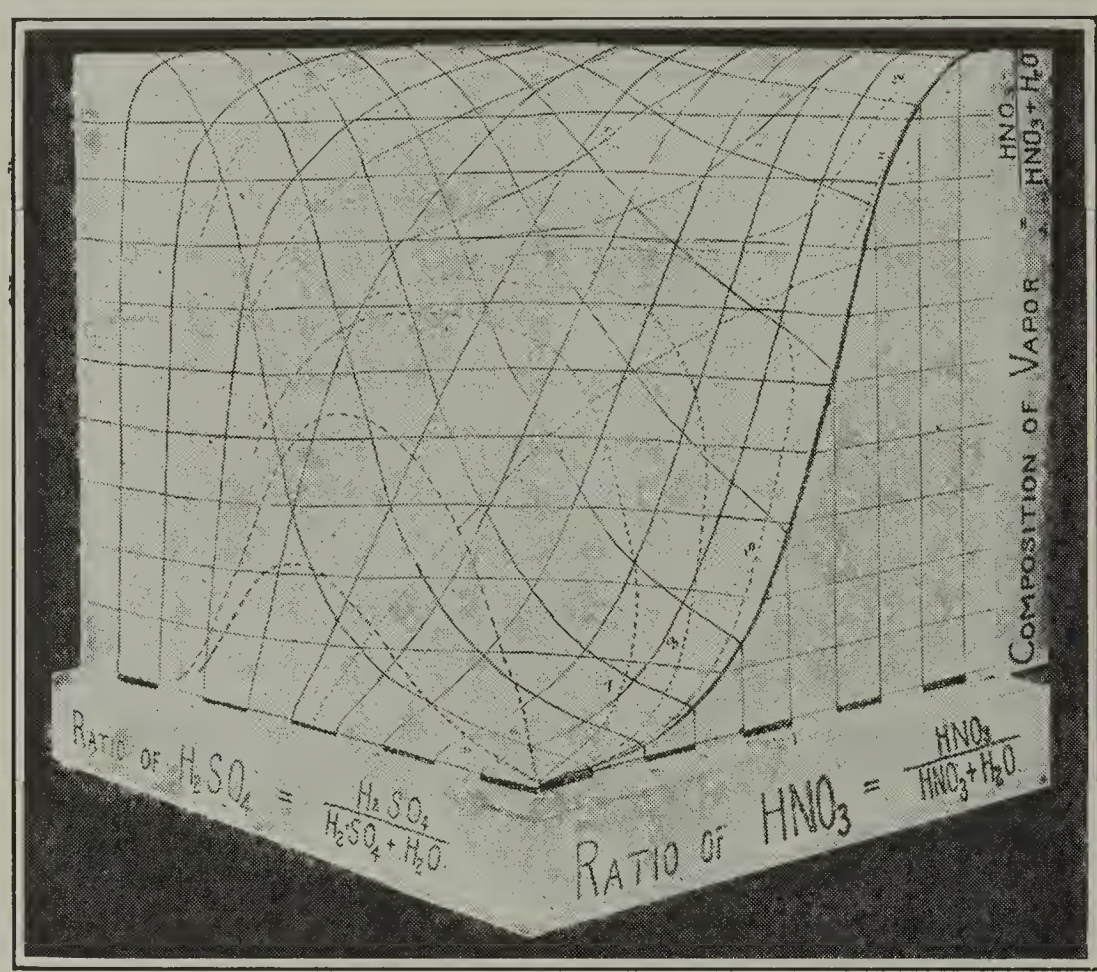


FIG. 8. Solid Model Showing Equilibrium between Liquid and Vapor Phases

as ratios of HNO_3 and H_2SO_4 along the *X* and *Y* axis, is represented by the base and the composition of the vapor in equilibrium with the boiling liquid phase is plotted as the vertical axis. The broken line curves in the solid diagram represent the distillation curves Nos. 3, 5, 7, 8, 10, 11, 12, 13, 14, 15 and 16 of Fig. 5.

The following information may be obtained from this model:

1. The composition of the vapor, or strength of the distillate, obtained by distillation without fractionation, of a mixture of nitric acid, sulphuric acid and water at any concentration of residue.

2. The change in the composition of the residue with distillation.

3. The change in the composition of the vapor with continuous distillation.

4. Starting with a dilute nitric acid solution, it becomes a simple matter to determine the amount of sulphuric acid to be added in order to obtain a distillate of a given strength.

It appears that an interesting relation exists between the points representing those solutions which are in equilibrium with a vapor whose composition corresponds to the ratio of HNO_3 in the boiling solution. In Figure 5 these points are indicated by circles through which a dotted line has been drawn. It is evident from the curves that in a solution, starting at 0 (hypothetical), and subjected to distillation, avoiding fractionation, the ratio of HNO_3 will reach a maximum and then decrease. At this maximum on the curve, the tangent to the curve at this point is perpendicular to the X axis and corresponds to a condition wherein the vapor leaving the solution has a composition equal to the ratio of HNO_3 in the liquid phase. These points, representing such solutions, lie on a curve which may be represented as approximately a portion of an ellipse whose equation is

$$\frac{x^2}{(68)^2} + \frac{y^2}{(45.2)^2} = 1$$

Table VIII shows the agreement between the ratio of sulphuric acid for a given ratio of nitric acid when calculated by the aid of the equation and when experimentally determined.

TABLE VIII

AGREEMENT BETWEEN EQUATION AND EXPERIMENT

Ratio of HNO_3	Ratio of H_2SO_4, Calculated	Ratio of H_2SO_4, Experimental
0.012	0.452	0.452
0.067	0.450	0.450
0.126	0.445	0.444
0.202	0.438	0.432
0.275	0.419	0.413
0.347	0.397	0.389
0.467	0.342	0.328
0.559	0.267	0.257
0.606	0.200	0.205
0.632	0.153	0.167

Another interesting observation shown in Fig. 5 is that only solutions having their origin to the right of the dotted line show this phenomenon. All other points have vapors richer in nitric acid than the residue.

The values represented in Fig. 6 are also plotted on triangular coordinates in Fig. 9 and curves 4, 5, 6 and 7 of Fig. 5 are plotted in Fig. 10. In Figs. 9 and 10 results of Berl and Samtleben are given for sake of comparison and are expressed by dotted lines.

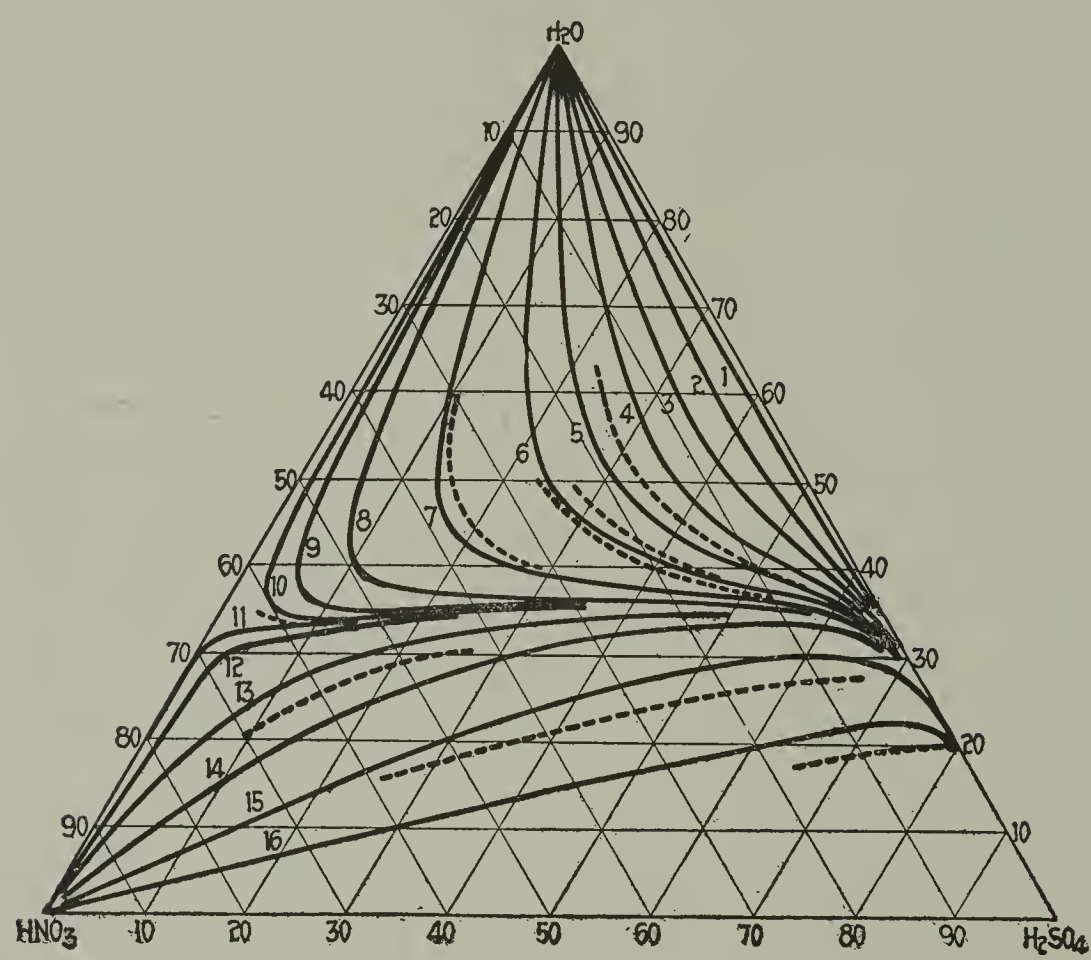


FIG. 9. Data of Fig. 5 Plotted on Triangular Coordinates

Here the discrepancies between their results and those of this work became very conspicuous. The differences are not so striking when the triangular coordinates are used as when the method adopted for representing the results of this work is employed. It becomes quite evident then that in the higher concentrations all precautions must be taken to prevent fractionation.

It seems from the regularity of our distillation curves that nothing except easily dissociable compounds between nitric acid and other components in the system exist at the temperature of distillation of the solutions. If there were, abrupt change of direction of the curves would take place, but this does not happen. It must be true however that the union between sulphuric acid and water is much more pronounced.

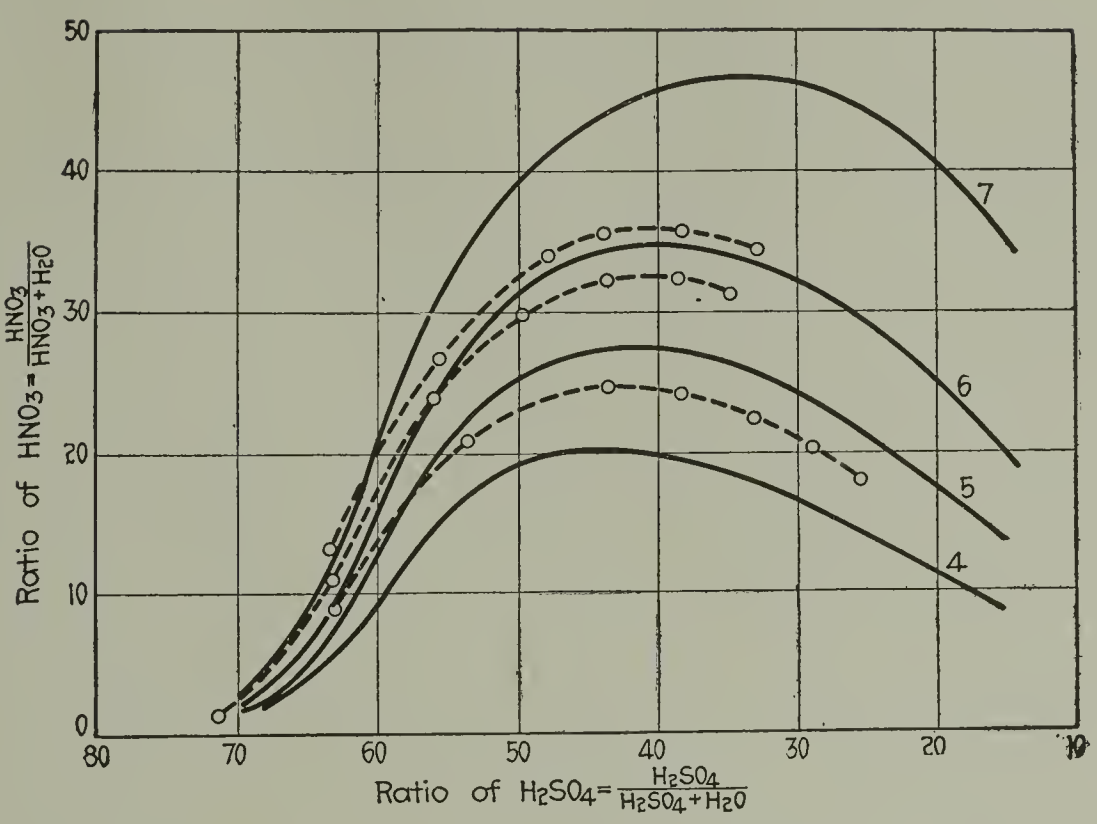


FIG. 10. Comparison of Data

SUMMARY

Extensive experimental data on the rate of concentrating nitric acid has been collected by distillation of various solutions of nitric acid, and of nitric acid, sulphuric acid and water solutions. It has been shown that the results are free from the errors caused by fractionation which has entered in the work of other investigators.

The greater accuracy of plotting the results on rectangular coordinates over that of the triangular diagram has been shown.

The data has been used to construct a solid diagram upon which the vapor in equilibrium with any liquid phase may be read directly.

It has been shown that a line connecting the points at which the vapor concentration is equal to the liquid concentration plotted on rectangular coordinates may be represented by an ellipse of the general form

$$\frac{x^2}{(68)^2} + \frac{y^2}{(45.2)^2} = 1,$$

when x = ratio of nitric acid and y = ratio of sulphuric acid.

The data therefore furnish an accurate basis for complete determination of all vapor liquid equilibria in the acid towers used in concentrating nitric acid solutions.

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CHEMICAL ENGINEERING ASPECTS OF WATER TREATMENT FOR RAILROADS

By WILLIAM M. BARR

Read at the Denver Meeting, July 17, 1924

To the theoretical chemist the whole explanation of water treatment may be written in the following equations:

1. $CaH_2(CO_3)_2 + Ca(OH)_2 \rightleftharpoons \mathbf{2CaCO_3} + 2H_2O$
2. $MgH_2(CO_3)_2 + 2Ca(OH)_2 \rightleftharpoons \mathbf{2CaCO_3} + Mg(OH)_2 + 2H_2O$
3. $CaSO_4 + Na_2CO_3 \rightleftharpoons \mathbf{CaCO_3} + Na_2SO_4$
4. $MgSO_4 + Na_2CO_3 \rightleftharpoons MgCO_3 + Na_2SO_4$
5. $MgCO_3 + Ca(OH)_2 \rightleftharpoons \mathbf{CaCO_3} + \mathbf{Mg(OH)_2}$
6. $Al_2(SO_4)_3 + 3Ca(OH)_2 \rightleftharpoons 3CaSO_4 + \mathbf{2Al(OH)_3}$

Now these, like all reactions, are reversible. Further, the speed of the reaction depends much on the temperature and pressure at which it takes place.

Consider what factors force their way into this problem when the temperatures vary from $-37°$ C. to $+193°$ C. and the pressures change from atmospheric to 200 lbs. per square inch. You would hesitate to operate a factory process with these variables and guarantee a product to satisfy the consumer. This is the first problem that confronts the chemical engineer in the treatment of water for locomotives.

These reactions are further influenced by the amounts and relative proportions of the various components in solution, as well as the physical character of matter in suspension.

The reaction temperatures of the water when treated range from slightly above 0° C. to 38° C. while the outside temperatures go down to $-37°$ C. It is obviously impractical to heat the water to be treated in order to hasten the reaction and make the precipitated solids settle more rapidly, since all of the heat is again lost when the water is stored and the cost would not be justified.

It is therefore necessary to precipitate the incrusting solids from the water without heating and at the lowest cost for chemicals, construction, operation and maintenance.

The first study for the chemical engineer before attempting the treatment of water supplies is the water conditions in relation to the operation of locomotives. The first concern of the operating official is to get trains over the road on time, and the next is to haul the largest tonnage possible. The movement of tonnage is the primary vocation of railroading. Therefore all work must be done with this end in view.

First, it is necessary to consider what waters are susceptible of treatment. The mere removal of the scale forming salts is only part of the problem, and many waters are unsuitable for locomotives after the scale forming ingredients have been removed. In such cases new waters must be developed wherever possible, and in some cases it is necessary to haul water from other stations at large expense, rather than attempt to use waters that may be available because these waters may seriously interfere with the movement of trains. There may be cases where it would be economical to distill a portion of the supply in order to reduce the concentration of dissolved solids. While the writer has found some cases where this has been considered, he has never actually made such installation, having found some other solution for the problem in these cases.

The greatest difficulty encountered with water by the locomotive engineer is foaming, as this invariably results in slowing down, and hence in delays. It is therefore necessary to produce a water that will show the least tendency to foam. Many water service engineers in the railway service advocate the over treatment of boiler feed waters, because by so doing the reaction is more complete and the scale forming solids may be reduced to the minimum. It is the experience of the writer that this method of treatment adds to the foaming difficulties of the engineer, and in certain localities, because of the mixing of treated and untreated waters, incrustation of the injectors and branch pipes gives trouble. It is therefore the policy of the writer to carry the water treatment as close to the end point as possible without carrying an excess either of caustic or carbonate alkalinity. Experience shows that this method has been successful and has resulted in a minimum of complaint from locomotive engineers from foaming. The amount of scale under this method of treatment is small, and the scale which forms is of soft carbonate character and is readily washed out of the boiler.

Even with this treatment we are compelled to use some waters

which have a tendency to foam. This is due largely to an excess of sodium salts, particularly sodium bicarbonate, which many of the natural waters carry. This condition must be taken care of by the use of an anti-foaming compound. Such a compound consists essentially of an emulsion of castor oil in water.

Corrosion is an evil we have always with us, and while it gives the locomotive engineer little concern, it must be carefully considered in the economy of boiler maintenance. The causes for corrosion are fairly well agreed upon. The difficult thing in the treatment of locomotive boiler waters is the prevention of this evil. If we could eliminate the dissolved gases, particularly oxygen, and hold the hydrogen-ion concentration to a minimum, the corrosion problem would be practically solved. A satisfactory method for bringing about this condition in locomotive supplies has not yet been worked out.

It is evident from what has been said that it is necessary for the chemical engineer to study conditions on the inside of the boiler when engines are in the shop, and also to familiarize himself with the operation of the locomotive by riding with engineers so that he may know the requirements that must be met with the treated water. The analysis of waters taken from the boiler at different periods furnishes much information of value in the control of locomotive supply. It was formerly the practice to change engines at intervals of approximately 150 miles. It has been found great economy can be effected by making the runs as long as possible, and without correct water conditions long engine runs cannot be made. It is now possible to run passenger engines 600 or 700 miles without change, and this is being done in normally bad water districts. It is only possible by correct treatment of the water and careful control on the locomotive by the chemical engineering force. A demonstration was recently made in which the writer took part to determine the possible performance of passenger engines. A mountain type engine was run west from the Missouri River 993 miles, pulling a full tonnage mail train, and without change of water made the return run with a similar train, making a total of 1986 miles continuous run without change of water in the boiler. Analysis of the boiler water upon arrival at destination showed satisfactory concentration, and the record of the engine showed practically perfect performance.

In the construction of water softeners a number of chemical

engineering problems arise. First, the satisfactory location of the softener in relation to other structures must be considered, in order to obtain the most economical operation of the softener. The treating plant must also be satisfactorily located with relation to the water supply to be treated. The water softener attendant usually has charge of the pumping plant, and being responsible for both plants, must have them so located that he can give both proper attention. In addition to this, the attendant in railway service may operate a coaling station. In this case it is necessary to have the water treating plant so located that the workman can give proper attention to both plants. This is not always possible, but in many cases considerable saving can be effected by proper location.

In constructing the plant, the type of softener is of great importance. Wherever it is possible, it is economy to build the softener so that the treated water flows by gravity from the softener into the storage tank, thus saving double pumpage. In cases

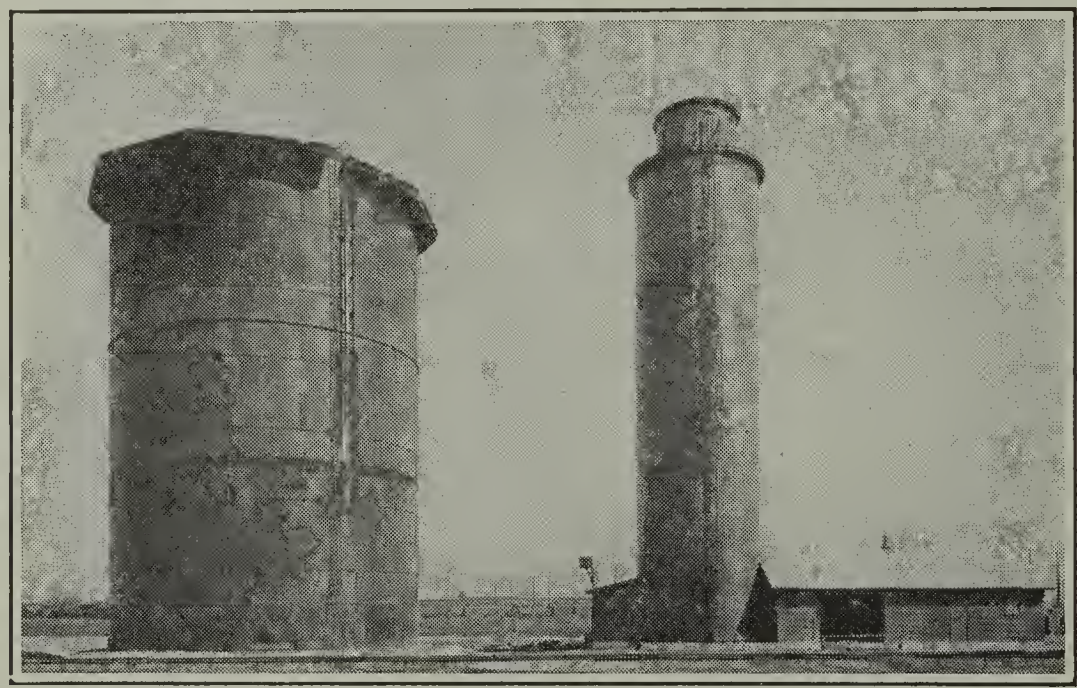


FIG. 1. Huge Water Softener at Council Bluffs, Ia.

This is the Union Pacific Terminal and the softener, a ground-operated type, has a capacity of 35,000 gal. per hour with 900,000 gal. storage.

where other conditions make it necessary to pump the water to the softener and then pump again to the storage tank, the most economical construction is the rectangular concrete tank, such as is commonly built for the treatment of small municipal water supplies.

The next thing to be considered is climatic conditions. Some

softeners are located where freezing weather is never encountered, and piping and machinery can be placed in the most convenient location as the temperature never interferes. In some of our northern climates where winter temperatures reach − 37° C. the greatest consideration must be given to this feature of water softener construction. Temperature has the greatest influence on the treatment because of the increased speed of the reaction with increased temperature. Therefore, in cold climates the softener should be designed with larger reaction space, as well as greater settling capacity. It has been found most effective to allow the chemicals to react for a period of at least 25 to 30 minutes before the settling process begins. If the chemical mixture and raw water are stirred during this period, better sedimentation is accomplished, thus giving a clearer water with a smaller settling capacity than if the chemicals and water are not stirred. Booth [1] showed the effect of stirring on precipitation of treated waters. The position has been taken by some engineers that if the water mixed with the chemical is allowed to plunge over baffles, thus obtaining a thorough mixing, reaction is satisfactorily accomplished. This, however, has a tendency to break up the precipitate, making it much finer than if the reaction takes place with a moderate stirring. If stirring is too rapid, there is also the same tendency to break up the precipitate. C. P. Hoover [2] has found that stirring at a rate of not to exceed .6 of a foot per second gives satisfactory results, but that this speed should not be exceeded. There are a variety of devices for bringing about this condition which are quite successful, but the softener should be so designed as to obtain the most nearly complete chemical reaction and produce the largest size particles in the precipitates so as to get the most rapid settling with good clarification of the water. Both the size and shape of the settling space are of importance. Where we are compelled to treat very cold waters it is advantageous to allow the precipitate to settle for six hours before attempting to deliver the water to the storage tank. In milder climates five hours are sufficient, and on waters that have a comparatively small amount of total dissolved solids with a low content of sodium salts and sulphate hardness, satisfactory results can be obtained in four hours. It is therefore apparent that the character of the water and the climate have an important bearing upon the cost of the equipment.

[1] *A. I. C. E. Transactions*, vol. 7.

[2] *Journal of the American Water Works Association*, vol. 11, No. 3.

Many times the water softener also serves for the removal of suspended solids, as with muddy waters, and if necessary to clarify these waters, a small amount of alum may be used, as is the practice

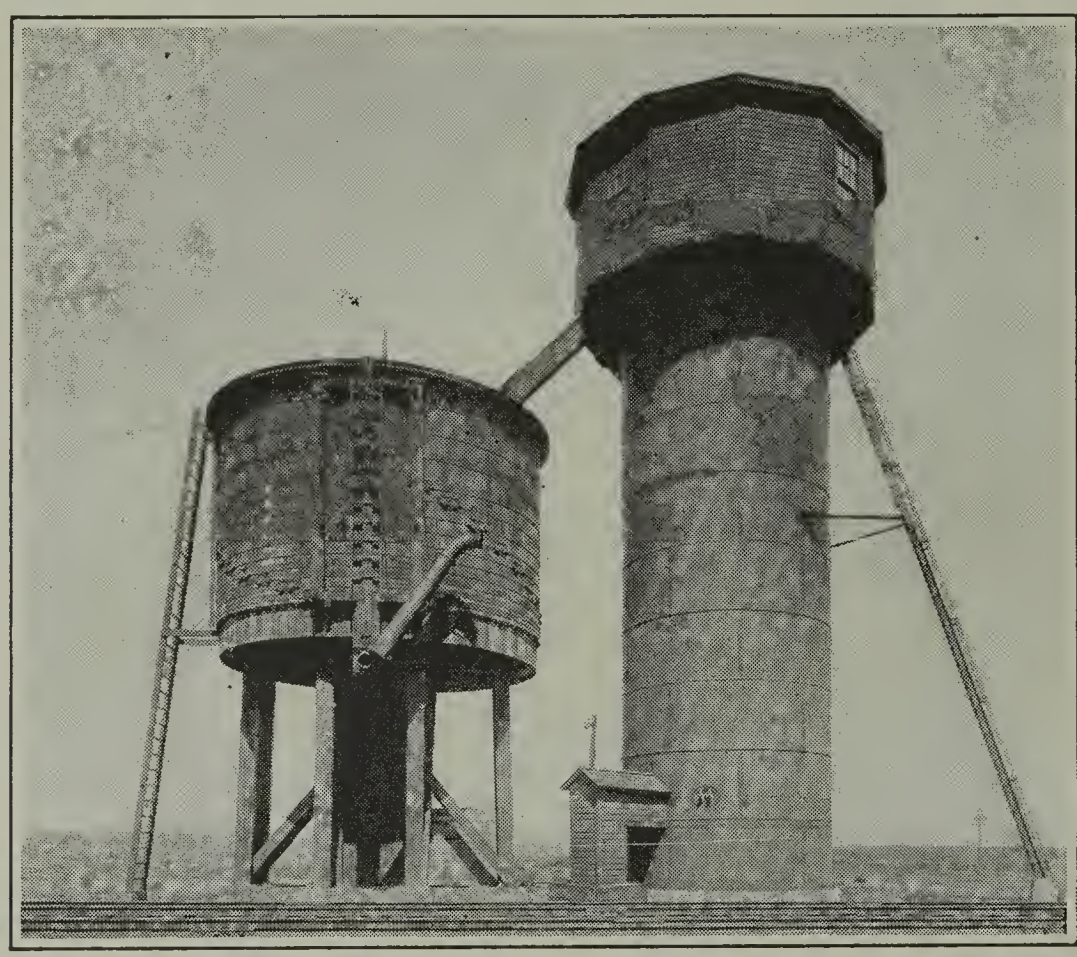


FIG. 2. Water Softener in Flat Desert Country.

Here at Cooper Lake, Wyo., the softener is infrequently attended and the climate is cold in winter, hence it is a top fed, housed type, with single lift.

in municipal filter plants. Many waters carrying high suspended solids can be clarified simply by lime-soda treatment if the character of the precipitate is such that it will carry down the suspended matter when settling.

The shape of the water softener is of some importance. While it is desirable to deliver direct from the softener to the storage tank, thus avoiding double pumping, this type of construction often gives the softener too small a diameter in relation to its height for correct reaction time, or requires the construction of a softener too large for the required service. In order to secure proper settling of the sludge, it is desirable that the rise of water in the softener should not exceed ten feet per hour, and in many cases a rate of eight feet per hour is more desirable. On the other hand, it has been shown that certain waters give a clear effluent

through an excelsior filter with a rise as great as fifteen feet per hour. It is often desirable to make settling tests upon the water to be treated before designing the treating plant. In order to make the full capacity of the treating tank effective, it is necessary that the water passing out of the downtake spread over the entire area of the softener. If the downtake is too small in relation to the diameter of the softener, water passing out of the downtake will create upward currents without spreading to the outside of the tank. This reduces the capacity of the softener.

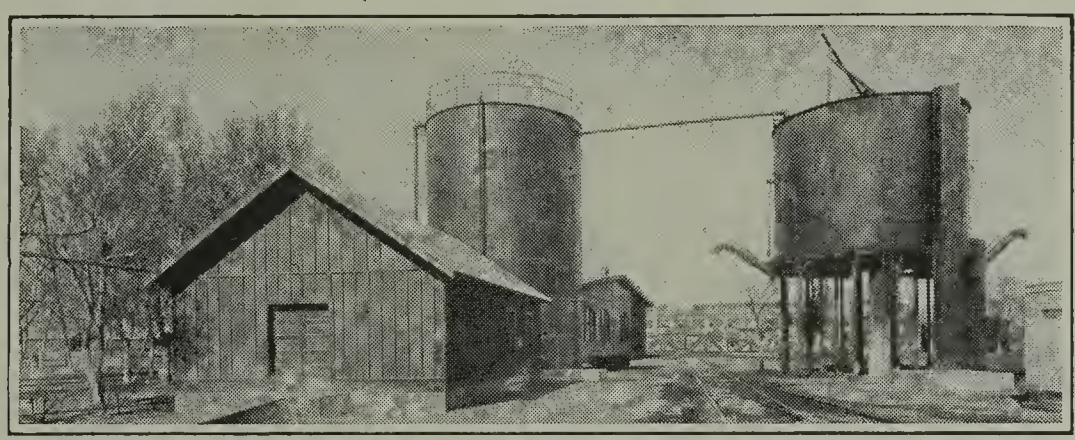


FIG. 3. A Warmer Climate Where No Housing is Necessary—Las Vegas, Nev.

There is a great divergence of opinion on the necessity for filtration of locomotive water supplies. The writer has built softeners without any filtration, with modern sand filters, and with a filter consisting of a twenty inch layer of excelsior, which is said to be nothing more than a strainer. Here is another feature that is purely a question of economy. Naturally the finest results can be obtained with a modern sand filter. This, however, is expensive in first cost, requires a considerable amount of water for back washing, needs increased attendance, and adds to the maintenance cost. Some waters can be sufficiently clarified for boiler purposes without any filter if the sedimentation capacity is sufficiently large. The writer's experience has been that wherever practical, a twenty inch layer of excelsior placed in the softener before the water discharges into the storage tank gives beneficial results. This acts as more than a strainer as the fine particles collect on the excelsior and it develops the character of a real filter. Waters which we have not been able to completely clarify without the so-called excelsior filter have been made perfectly clear by its use. It is necessary to renew the excelsior at intervals varying between six months and a year, depending upon the filter capacity. This is the lowest possible maintenance cost for any character of filtration.

In the construction of steel equipment for water softening the chemical engineer must give consideration to the life of the different parts of this steel construction, as well as to strength of riveted joints, weight of load on foundation, wind pressures, and other more strictly engineering features. Treating plants that have now been in operation for twenty-one years or over, indicate that for most waters there is very little corrosion of the steel inside the softener below the water line. In many cases there is considerable corrosion of the top sheet at the water line. It is therefore good practice to slightly increase the thickness of the top sheet to allow for such corrosion. It is also the writer's practice to make the bottom of the softener of extra heavy plate, as it is difficult to prevent some corrosion on the under side of this sheet, and it is

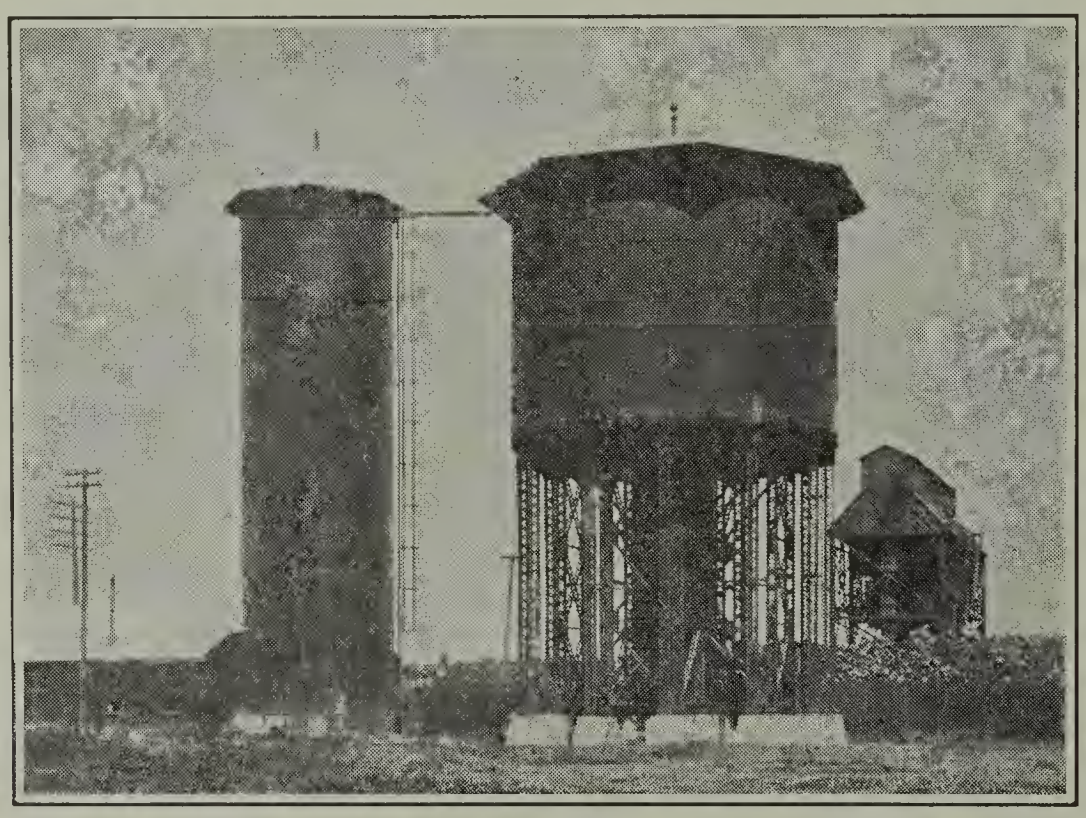


FIG. 4. Another Large Softener.
18,000 gal. per hour, ground-operated at coaling station, Junction City, Kan.

extremely difficult to replace this part of the machine. On account of corrosion of parts above the surface of the water, it is desirable to make eye-beams and other structural steel in such places of greater weight than mere strength requirements would call for.

If it were possible to treat waters in exact accordance with the equations already shown, the problem would be a very simple one. Theoretically it should be possible to remove the incrusting solids to the point of solubility of calcium carbonate in cold water, as

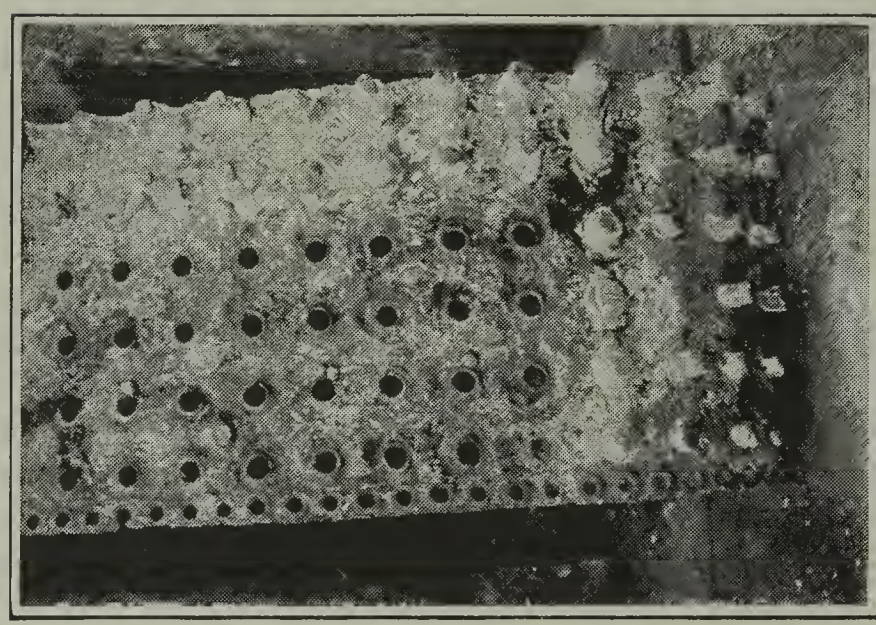
this is the form in which most of the material is precipitated. According to Olsen,[3] calcium carbonate is soluble in cold water to the extent of thirteen parts per million, and magnesium hydrate, in which form the magnesium salts are precipitated, is soluble to the extent of nine parts per million.

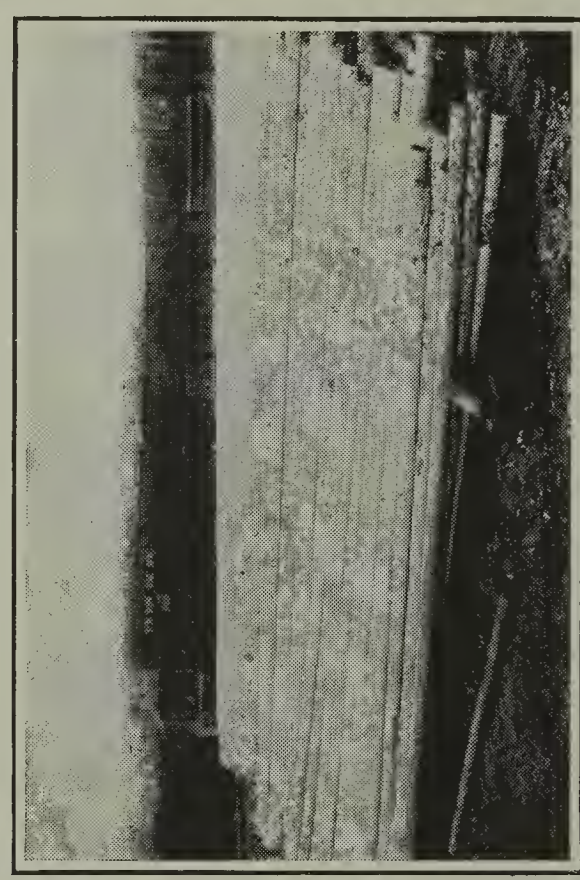
In waters having a moderate temperature—that is, 15° to 25° C. —with a thirty-minute reaction time and five hours settling, some waters can be treated as low as fifty-five parts per million. In the experience of the writer, they rarely go below this. While it is frequently asserted that all conditions being equal, the hardness of water can be reduced further by carrying an excess of both caustic and carbonate alkalinity, we frequently find that certain waters can be treated to fifty-five parts of hardness per million without carrying any excess of the precipitant. On the other hand, we frequently find waters with an overtreatment in which the hardness cannot be brought nearly as low as this. A certain water under exactly the same conditions of temperature, reaction time, and settling space, as the one shown above, gave a hardness of ninety parts per million and carried an excess of both caustic and carbonate alkalinity.

When the question of winter temperatures is considered, we find it still more difficult to reduce the treatment to the desired limits. Certain waters carrying considerable amounts of calcium sulphate and magnesium sulphate in addition to calcium carbonate in solution, when treated in accordance with standard practice with outside temperatures from − 15° to − 20° C., and the water itself just above freezing, gave a hardness of 150 parts per million as it left the softener, and showed by the alkalinity and causticity that sufficient chemicals had been added to react completely with the calcium and magnesium salts. This same water after standing in a storage tank seven hours still showed 150 parts per million of calcium carbonate, or equivalent, in solution. It is evident that when a water of this kind passes into the locomotive boiler and is heated to a temperature of 194° C. under pressure of 200 lbs., that this reaction will be quickly completed and the precipitate will be thrown down in the boiler. Such a condition has a tendency to aggravate foaming and must be relieved by frequent blowing off of the boiler.

Since the range of conditions is so variable, and it is therefore

[3] Van Nostrand's Chemical Annual.





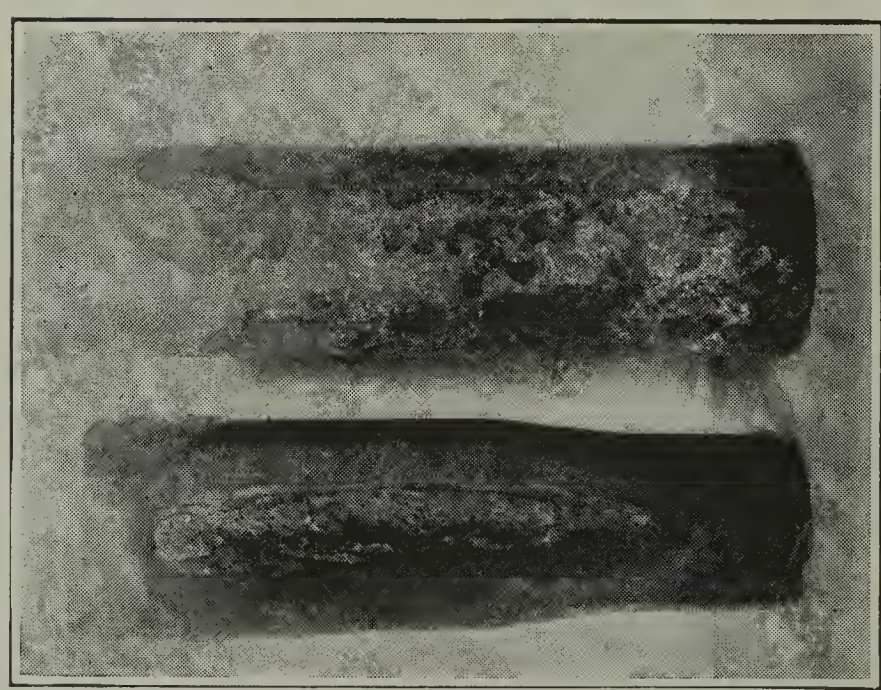
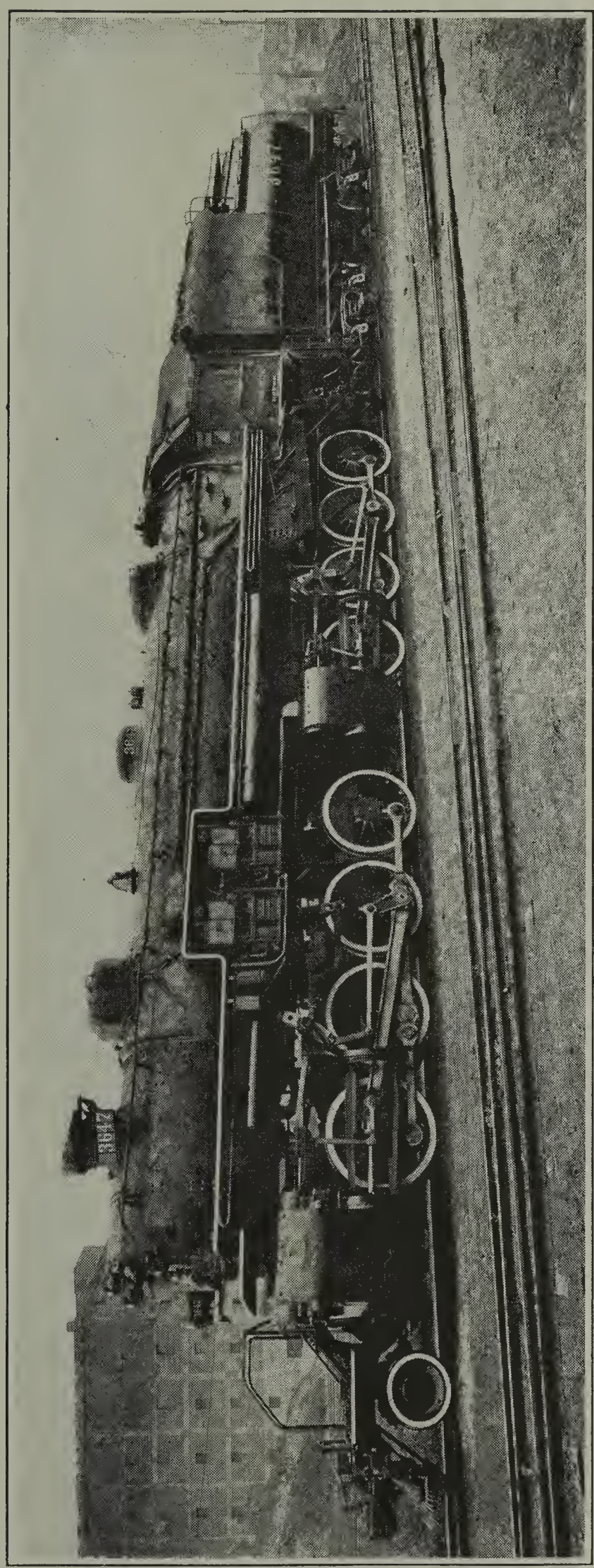


FIG. 5.

At left—Sections of boiler tubes after scale has been removed, showing pitting and corrosion that takes place.

At center—Locomotive tubes with heavy scale. This shows how the rate of heat transfer is cut down and efficiency lost on account of scale formation.

At right—Boiler plate, showing scale formation.



Modern Type of Locomotive Used by Union Pacific R. R.

necessary in many cases to have a considerable quantity of the scale forming salts remaining in solution, it has been the practice of the writer to avoid the addition of excessive amounts of lime and soda ash at all treating plants. This avoids the difficulties referred to with incrusting of injectors and branch pipes, holds the foaming tendency to a minimum, and at the same time gives a water which operates satisfactorily in locomotives, keeping the flues and fire boxes clean. From such treatment the maximum efficiency of the fuel is also obtained, and fuel losses due to excessive use of the blow-off on account of foaming are prevented and heat transfer is made efficient by keeping the tubes clean.

The question is frequently asked, "Why do you not use zeolite water softeners on railroads?" A zeolite softener removes the scale forming salts by exchanging the sodium content of the zeolite for calcium and magnesium content of the water. This results in what the manufacturer refers to as zero hardness because of the complete removal of the calcium and magnesium from the water. However, there must be in the treated water a molecular equivalent of both sodium bicarbonate and sodium sulphate replacing the calcium and magnesium becarbonates and calcium and magnesium sulphates in the original water. As nearly all of the naturally hard waters carry a considerable amount of carbonate hardness, it is evident that the treated water will carry a similar amount of sodium bicarbonate. This would invariably aggravate foaming, not only making operation expensive, but resulting in great dissatisfaction among the men who handle the engines.

Sodium aluminate has recently been put on the market for use in water softening. This material has always been considered prohibitive on account of cost. This cost is still high as compared with the use of lime and soda ash. There are, however, some cases where this material can be used to advantage. It reacts quickly in the cold, forming a flocculent precipitate which in cases of muddy waters takes the place of alum and at the same time acts as a softening agent. Experiments conducted by the writer showed that the use of sodium aluminate combined with lime and soda ash gave a hardness of 70 parts per million as against 90 parts per million, which was the best we were able to obtain with straight lime-soda treatment. These experiments were carried out on a very hard cold water at an increased cost of 10 per cent over the straight lime-soda treatment.

A considerable amount of careful and painstaking laboratory work has been done on boiler feed waters which does not permit of practical application, particularly to locomotive boilers. It is obviously impossible to maintain chemical control on the locomotive. Therefore the chemical engineer must maintain his control largely at terminals. Owing to the conditions peculiar to railroad service, the problem of water supply and treatment is much more complicated than in the case of stationary power plants, using a single supply with a laboratory close at hand.

The problems in railway water supply are many and varied, as each water station offers an individual problem for the chemical engineer. It has been the object of this paper to call attention to enough of these problems to make it clear that the treatment of railway water supply is peculiarly one for the chemical engineer rather than the laboratory chemist.

REFINED SULPHURS: THEIR MANUFACTURE AND USES

A Comprehensive Review of the Development and Present Status of the Sulphur Refining Industry, and a Critical Summary of the Properties and Commercial Application of the Different Forms of Refined Sulphur

By CHARLES A. NEWHALL,

Read at the Denver Meeting, July 17, 1924

It is to be owned that many things have been writ of Sulphur; but the true Foundation of the Virtues thereof has scarcely yet by man been exactly enough touched or proposed.

Whosoever shall attempt to describe Sulphur in a most accurate manner (as is fit, tho not expedient) will have need of abundance of paper.

—From an ancient writer quoted in "Sulphur and Sulphur Derivatives" by H. A. Auden; Sir Isaac Pitman & Sons Ltd. London.

Since these words were put on paper many centuries ago, very much has been added to the "many things that have been writ of Sulphur." Yet it is surprising how little there is of record concerning the commercial and technical aspects of the refined sulphur industry. Perhaps in the past those engaged in the industry have felt it was to their interests to be reticent rather than to use an "abundance of paper" in setting forth the virtues of their product; they trusting no doubt that the recognized merits of refined sulphur would be sufficient to sell the output of their refineries.

The use of refined sulphur is increasing steadily and rapidly. American refineries turn out something like 50,000 tons of refined sulphur per year and foreign refineries probably double this tonnage. Thus the use of refined sulphur accounts for considerably over ten per cent of the total world sulphur consumption estimated at about one million tons per annum. The American refineries and

those European ones about which I have information have their output well disposed of and their refining equipment is being enlarged. Yet within recent years a considerable controversy has arisen as to the merits of refined sulphur as compared with other grades manufactured directly from crude sulphur without refining. This controversy is hurting all branches of the sulphur industry and, if continued, is certain to retard materially the normal increase in sulphur consumption. To my way of thinking this controversy is largely due to a lack of understanding within the industry as to the physical and chemical properties and the proper uses of the different grades of refined and crude sulphur. In this paper I will endeavor to point out the essential differences in the several sulphurs that enter into commerce; dealing especially with the refined grades as the crude forms have already been ably described in the *Proceedings* of the Institute. In doing this something must be said about the construction and operation of sulphur refineries, although I must confess that my remarks on this ancient and very interesting phase of the sulphur industry will be but general in nature as matters of expediency still govern the public discussion of this part of the subject.

The most thorough paper published in recent years on the sulphur industry was read before members of the Institute at the New Orleans Meeting.[1] However in this very interesting paper but little is said about the use of refined sulphur. The article tends to leave the impression that the raw sulphur as produced in the Gulf fields is suitable for most if not all purposes. Other interesting reports on the origin, occurrence and production of crude sulphur appear in the U. S. Geological Survey publications and in Mineral Industry.[2] Guttmann[3] gives a good description of the sulphur refining processes as followed in France and England. Molinari's[4] account of the Italian practice of sulphur extraction from the ore and the refining and manufacturing processes is quite complete.

[1] "Recent Advances in the American Sulphur Industry," by R. F. Bacon and H. S. Davis, *Trans. Am. Inst. Chem. Eng.*, vol. XIII., Part 2.

[2] U. S. Geological Survey Bulletin 260, page 589; same Bull. 340, page 451; *Mineral Industry*, vols. 30 and 31; these being of special interest.

[3] "Manufacture of Explosives," by Oscar Guttmann; Whitaker & Co., London.

[4] "Inorganic Chemistry," by Ettore Molinari; P. Blakiston's Son & Co., Philadelphia.

He describes some seventeen commercial varieties of sulphur that enter the Italian trade; each having very distinct properties and uses. Lunge[5] gives a thorough review of the literature that concerns the production, refining and testing of sulphur. In this review a number of patents are cited wherein the inventors seek to improve the old standard process of refining sulphur. As far as I can learn no sulphur refiner of any consequence in the industry has adopted any of these proposals. Therefore, I will not discuss them; interesting though many of them appear to be.

The Industry in the Past

The principle factors in the sulphur industry still follow the ancient methods in use for hundreds of years. Nearly four centuries ago Robert Boyle, in his "Sceptical Chymist," quite accurately though briefly describes the essentials of sulphur refining: "Common Sulphur (if it be pure and freed from its vinegar) being leasurely sublimed in a close vessel, rises into dry flowers, which may be presently melted into a bodie of the same nature with that which afforded them." During the centuries in which refined sulphur has been an indispensable article of commerce, the refining process has remained essentially the same though there has been a gradual increase in the size of the "close vessel" or retort as we now term it.

Figs. 1 and 2 show two forms of French sublimers. As described by Guttmann these sublimers consist essentially of iron retorts which hold several hundred pounds of molten sulphur; these retorts being filled from a kettle which is used to melt and dry the crude sulphur. Each retort is connected with its condensing chambers by an iron flue which serves as a sort of reflux condenser. One type of retort is described as a simple cylinder 20 in. in diameter and 5 ft. long. Another type of retort is lenticular in cross section.

The condensing chamber is described as being square and of about 3000 cu. ft. volume. It is equipped with a heavy safety valve. When the temperature in the chamber is kept below 100 deg. C. flowers of sulphur are deposited. If the temperature is

[5] "The Manufacture of Sulphuric Acid and Alkali," by George Lunge; 1913 edition, vol. I., part 1, and vol. I., part 3 (Addenda). D. Van Nostrand Co., New York.

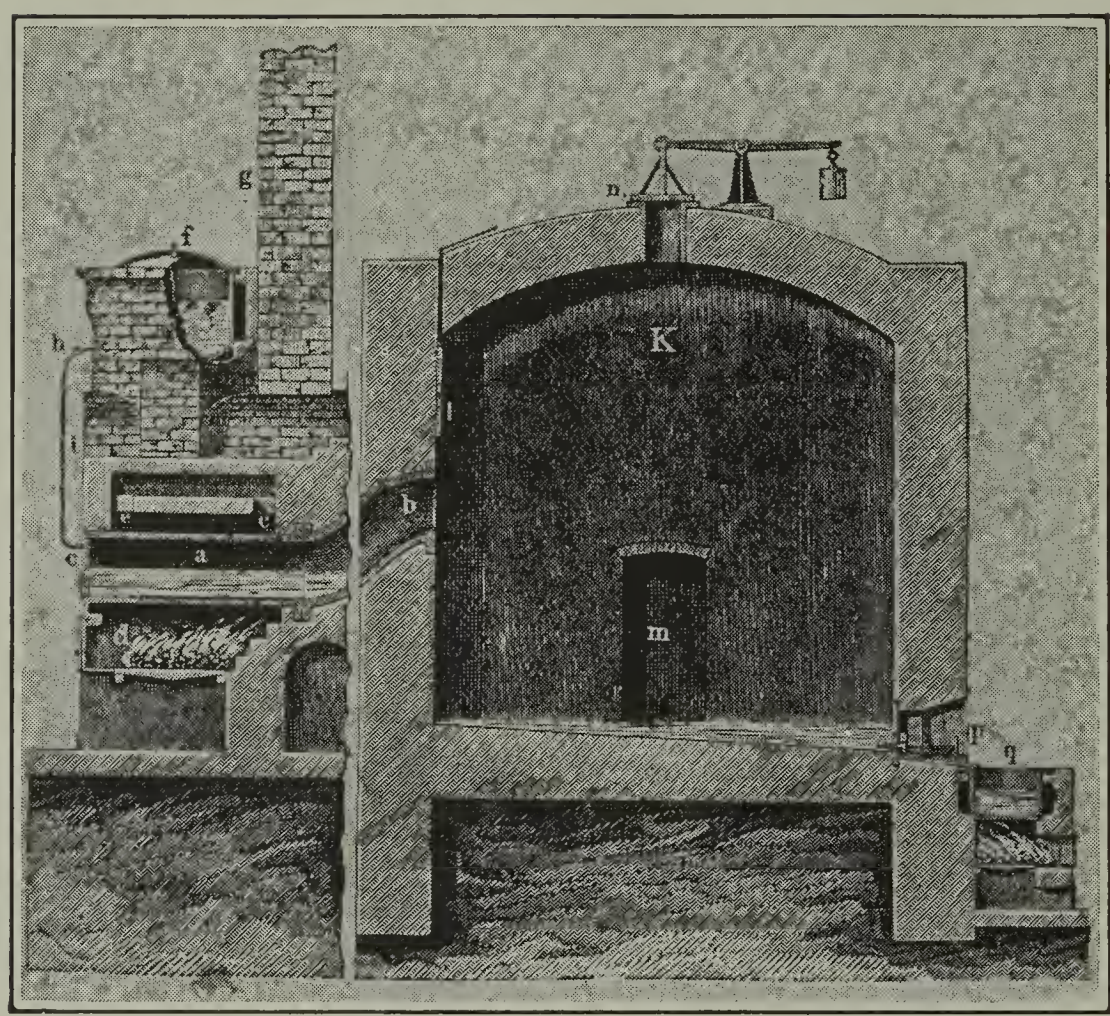


Fig. 1. A French Sulphur Sublimer after Guttman.

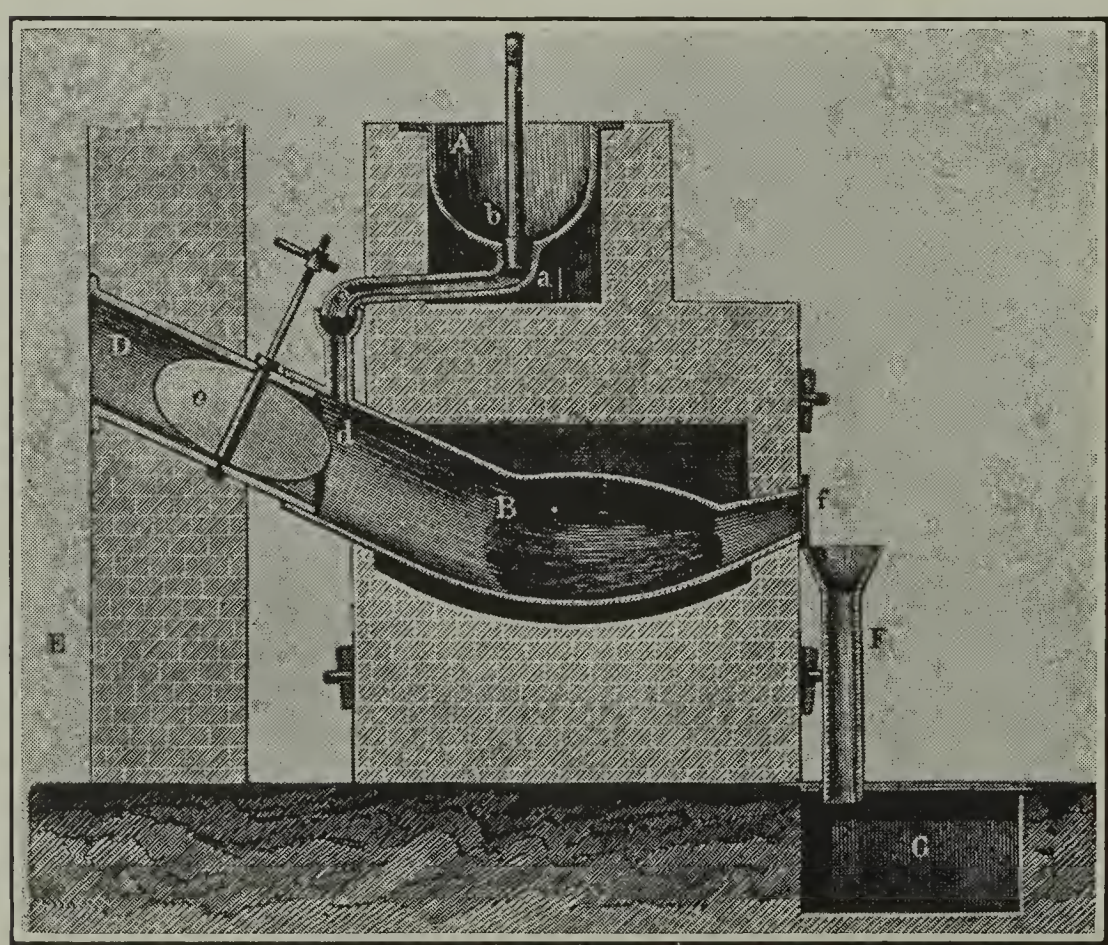


Fig. 2. Modified French Sublimer (from Guttman).

allowed to rise higher than 100 deg. C. the sulphur vapor condenses as liquid and is drawn off and cast into blocks.

The Italian equipment discussed by Molinari is similar to Fig. 1, as described by Guttmann. Two retorts subliming into one chamber produce about 1.8 tons of sublimed sulphur each 24 hrs.

Guttmann describes an English sublimer, Fig. 3, that is quite different in construction from the French and Italian type. This English equipment is apparently adapted principally to the production of brimstone rather than flowers. In the figure *a* is a metal

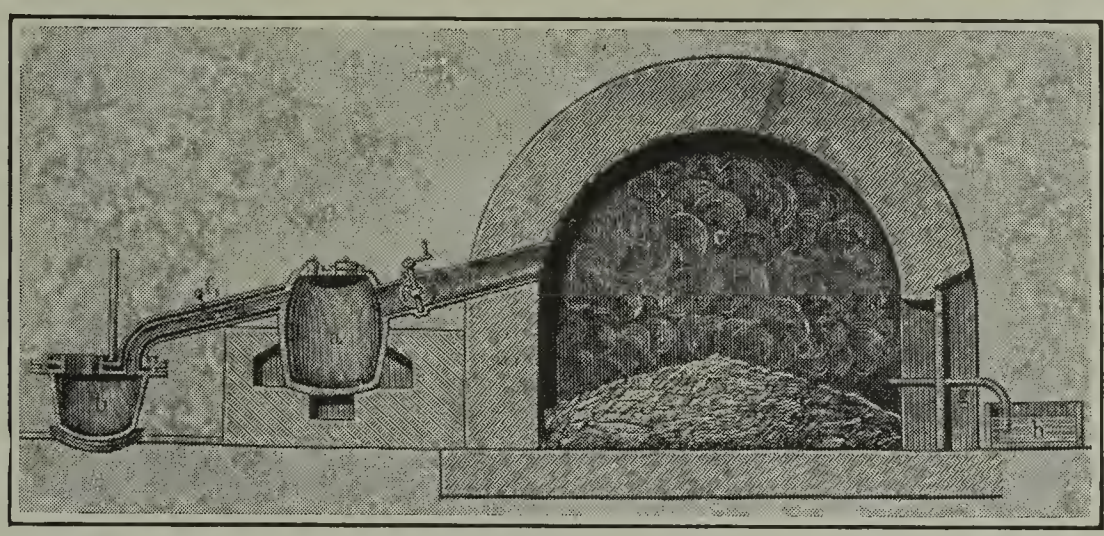


Fig. 3. An English Sulphur Sublimer.

kettle containing the molten sulphur. As the temperature rises the sulphur vapor first formed is carried through the large pipe *e* into the condensing chamber *c* in which the sulphur deposits as flowers. As the temperature in *a* rises and the vapor becomes heated the valve *f* is closed and *f1* is opened thus diverting the sulphur vapor into the pot *b* where it condenses as molten sulphur. The molten sulphur is baled out and cast into blocks. The flowers which contain acid and are thus unsuited for explosive work are remelted along with raw sulphur.

The Industry of Today

Fig. 4 shows the exterior of a small modern refinery and indicates the massive type of construction that is essential if a high grade product is to be produced. Figs. 6 and 7 show interior views of the sublimer room. Fig. 5 shows diagramatically a modern sulphur sublimer. The crude sulphur is dumped into the kettle where it is melted by heat from the furnace. The molten

sulphur, after being freed from moisture and the light impurities which rise to the surface and are skimmed off in the kettle, is dropped through the plug valve into the retort. This retort is flat

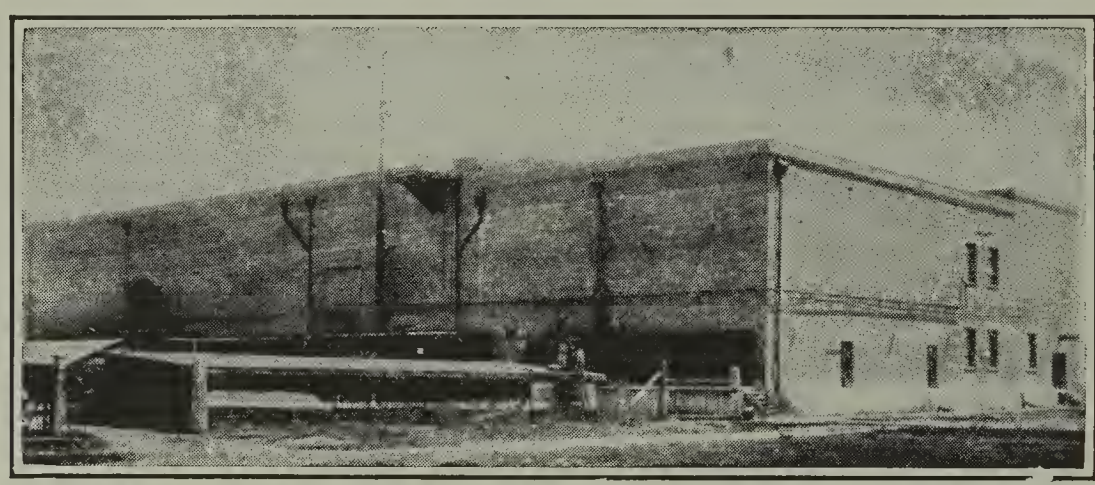


Fig. 4. A Small Modern Sulphur Refinery.

bottomed and arched at the top in shape much like the fireclay muffles used in the benches of the old-style gas producers. The front end of the retort is equipped with a cleaning door and with

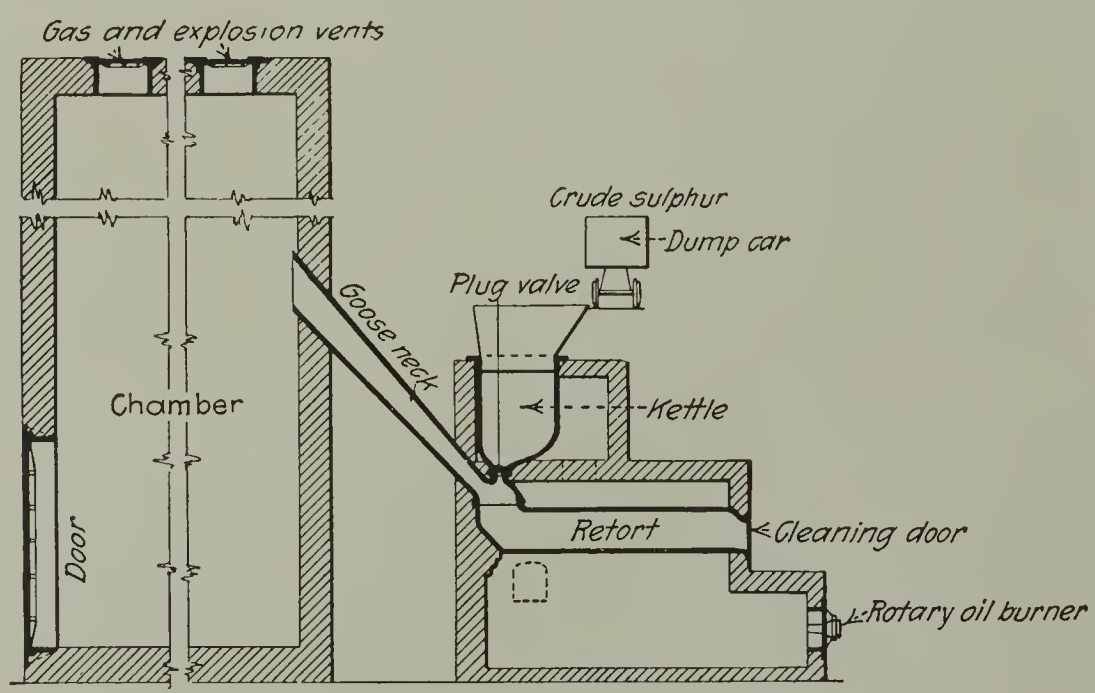


Fig. 5. Modern Sulphur Sublimer (Diagrammatic).

suitable plug cocks for testing the level of the molten sulphur within the retort. The sulphur vapors rise through a long "goose neck" and enter the chamber.

The chambers in a modern refinery are immense vaulted rooms of volume up to 30,000 cu. ft. or more where flowers of sulphur are

the desired product. Where roll sulphur or brimstone is the product desired the chambers are small affairs similar to the European type described by Guttman and Molinari.

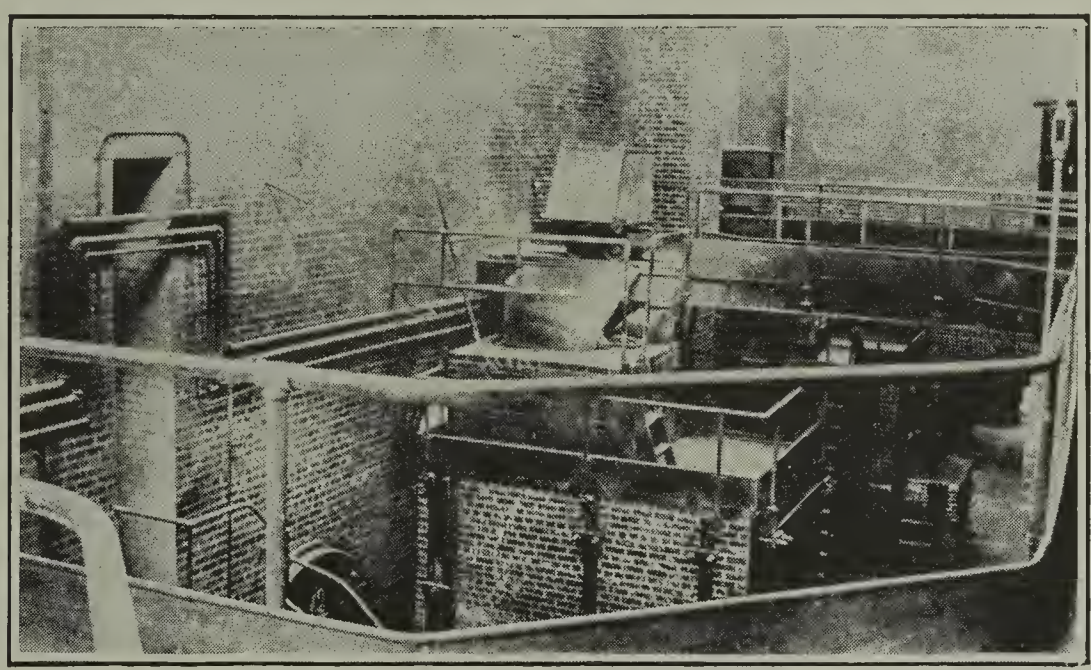


Fig. 6. Sulphur Refinery showing Charging Hopper and Kettle over Retort Housing.

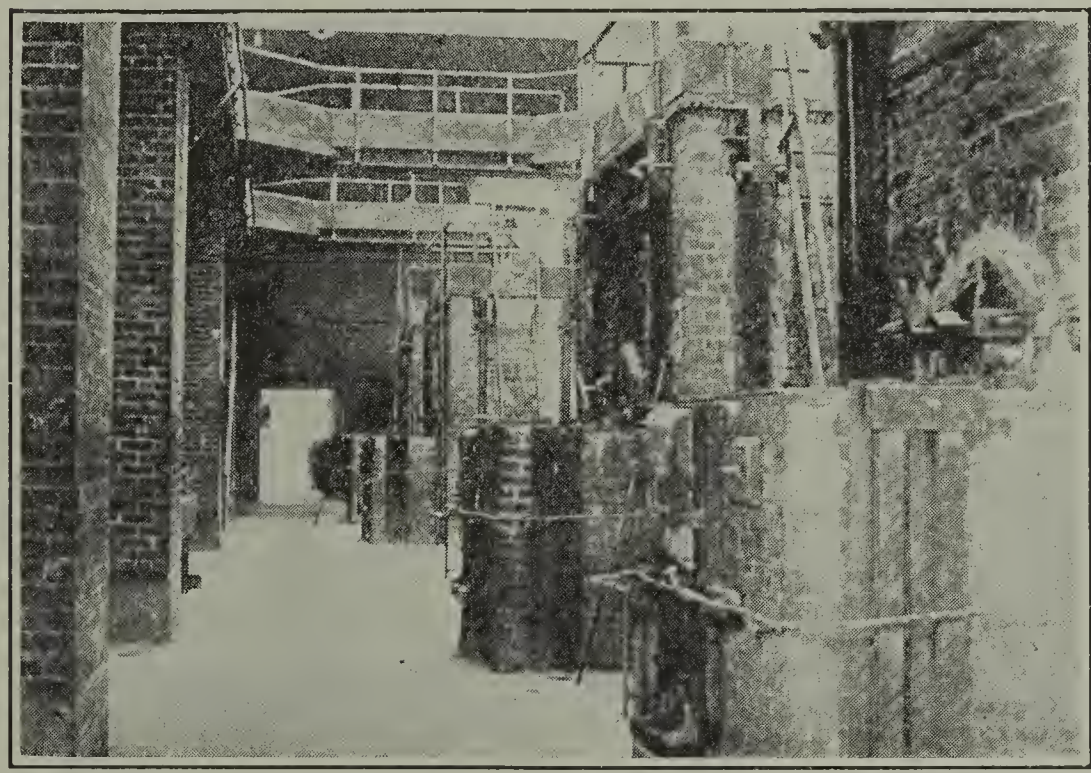


Fig. 7. Retorts (Cleaning End) and Furnaces.

In the construction and setting of the kettle, retort and goose neck, extreme care is exercised to guard against breaks and leaks. Special construction is used to make the chambers practically vapor

tight. Sulphur vapor and sulphur dust are explosive and flammable in the extreme and therefore leaky equipment must be guarded against. Another danger that is unusually troublesome in sulphur work is the action of static electricity which is the cause of fires and explosions at frequent intervals. This source of trouble apparently can not be entirely prevented but the effects can be confined to small units and thus great damage avoided.

A single sublimer unit producing approximately 4 tons of sublimed sulphur each 24 hrs., together with the essential accessory equipment to convey, pulverize and pack the products, costs something like $50,000. The largest refinery I know of consists of 7 units for producing flowers and one unit for producing brimstone or roll sulphur.

Refining Operations

In making sublimed sulphur the operating cycle consists in melting the sulphur, skimming, subliming, condensing, "gassing" or cooling the chamber, unloading the chamber and finally cleaning the residue from the retort. The operations are so balanced and conducted that one cycle follows another in practically continuous succession from month to month until a leak develops or a retort cracks or like trouble that calls for a shutdown and repairs. Of course the operation varies somewhat depending on the kind of crude sulphur being worked.

In the first step of melting the sulphur the temperature must be raised high enough to drive off all moisture and volatile acid or the "vinegar" as Boyle terms it. Also this step should char the organic matter present in the sulphur, yet the temperature should not be raised so high as to make the sulphur pass into the viscous modification as it would then be difficult to handle. Moisture and volatile matter if allowed to enter the retort with the sulphur will cause spurting during the subliming operation.

In the second operation of skimming, the reader would be surprised to see the volume of asphalt and wood that is taken from even the "99.5 per cent pure" crude sulphur from the Gulf fields which is the product now mostly refined. Formerly Italian and Japanese sulphur was the principal crude refined on the Pacific Coast but now no Italian crude comes in and only occasional shipments of Japanese. Naturally the source of the sulphur and the

impurities present determine the amount of material removed at this step.

The most difficult operations in the whole cycle are the "subliming" or boiling and the condensing of the sulphur. This subliming is carefully watched by experienced operators and is checked by indicating pyrometers in the most modern plants. The splendid research of Alexander Smith[6] and his associates has done a great deal to explain the behavior of sulphur when heated to high temperatures and then suddenly cooled. As far as I am aware the sulphur industry, strange to relate, does not know of this beautiful piece of pure scientific research. Yet the practical application of many of the points investigated would undoubtedly mean millions of dollars each year added to the income of the sulphur producers and refiners and at the same time would give the sulphur consumers a superior product.

Some of the points made clear by Dr. Smith and his workers have been discovered through the very costly cut and try methods many years ago in the sulphur industry. For instance it has long been recognized that the presence of sulphur dioxide was needed in the chambers in order to secure the highest quality flowers. It has also been known that the temperature and velocity of the sulphur vapor on entering the chamber had some bearing on the quality of the product.

During these third and fourth stages of the cycle the operator can control the percentage of "acidity" that is developed in the flowers of sulphur. This percentage of acidity has an important bearing on the value of the product. Acidity in terms of H_2SO_4 is usually held between 0.20 per cent and 0.50 per cent when the flowers are to be used in the agricultural districts for control of mildew and insect pests by the dry dusting method. The acidity could be run up much highed by proper methods but such high acidity would cause the containers to corrode and also would develop a poor mechanical behavior in the dusting machines. Irregular acidity is one of the bad features of a poorly operated refinery.

When the doors and vents of a chamber are unsealed it is found

[6] University of Chicago Decennial Publications, 1st series, vol. 14, page 55; *Berichte,* vol. 35, page 2992; *J. Am. Chem. Soc.,* vol. 27, page 797; same, vol. 29, page 1032.

that the finest, fluffiest, "velvety" flowers containing the highest percentage of amorphous sulphur are deposited at a distance from the goose neck. Nearer the goose neck the flowers are heavier and "rougher." Directly under the goose neck the sulphur is in a solid mass like frozen snow or ice. In some refineries the entire content of the chamber is mixed together and after running through beater type mills and being bolted is sold as sublimed flowers of sulphur; this practice gives a very inferior product, however.

In the larger refineries the content of the chamber is very carefully separated into three or more grades. Only that material is marketed as flowers of sulphur that shows a bulk of over 74 deg. Chancel,[7] or as packed in bags or barrels a bulk of about 30 pounds per cubic foot, and a content of amorphous sulphur of at least 30 per cent.

The heavier material from the chambers is run through granulator and beater mills and bolted or air (or gas) separated or sold in lump form. The bolted product is sold under the trade designations (American Pacific Coast) "Flour Sulphur" or "Powdered Sublimed Sulphur"; the air separated product as "Ventilated Sulphur" or in the East Coast markets as "Superfine Refined Sulphur"; while the heavy product is marketed under the various designations of "Heavy Flowers," "Refined Lump," "Virgin Lump," "Lump Brimstone" and the like. As stated before, Molinari gives 17 distinct types of sulphur sold on the Italian market. Other markets have an equally confusing number of designations and in fact each trade has its own designation for the types of sulphur used. For instance the fumigating trade can use a "Refined Lump Sulphur" carrying a rather heavy arsenical content whereas the Hop Bleaching Trade must have an arsenical content below ten parts per million. In the first trade the presence of minute amounts of asphaltic matter is of but little consequence as the sulphur is burned under heat, whereas even 0.004 per cent of asphaltic matter in the sulphur will cause trouble in the fumigating trades where sulphur must be burnt in open dishes and without undue heating.

In making the sublimed flowers of sulphur in the big chambers

[7] For Chancel's Test see Lunge, "Sulphuric Acid and Alkali," vol. I., part 1, page 47 (1913 edition).

the time of the subliming step is so regulated that the desired proportion of high grade flowers is produced in each cyycle. A well operated sublimer should turn out at least 50 per cent of the highest grade flowers and the balance divided about equally between lump sulphur and the heavier flowers. A chamber could be operated to turn out 100 per cent flowers of the highest grade but such operation would not usually be profitable under the ordinary commercial conditions.

When the purpose of the subliming operation is to make refined brimstone or roll sulphur the small chamber is used and the temperature within kept close to the melting point of sulphur. Often this grade of sulphur is made by remelting and resubliming the heavy grades from the big chambers. The chamber is not opened at the end of the subliming stage but the liquid sulphur is drawn off from the sump of the chamber as fast as the sulphur is either cast directly into the conical three pound sticks and sold as roll sulphur or brimstone or it is run into blocks and cooled. These blocks are broken up and granulated, pulverized in beater type mills, bolted or air separated and sold to the trades that require an acid free 100 per cent rhombic product. In this operation of making refined brimstone the essential operations are concerned with the removal of all moisture and acidity and the production of 100 per cent rhombic sulphur instead of the production of as high as possible percentage of amorphous sulphur as is the case in making flowers.

So far in this paper I have described the manufacture of refined brimstone and the manufacture of flowers of sulphur. A third form of refined sulphur commonly called "precipitated sulphur" enters commerce in limited amounts. This form is made not by sublimation but by precipitation from soluble polysulphides. In the drug trades this form of sulphur is called "Magister of Sulphur" or "Lac Sulphur."

While this precipitated sulphur has but little interest for the refiner on account of the limited amount used it is of much interest to one studying the physics and chemistry of sulphur. In passing I should also note that, indirectly, this form of sulphur is of immense importance to the agriculturist as it is this form of sulphur that is deposited on the plant after spraying with Lime Sulphur Solution and is the lethal agent of this important insecticide and

fungicide. However lime sulphur and other sulphur combinations used in agriculture and industry call for a separate paper as their manufacture and uses do not properly come under my present subject.

Commercial Applications

In discussing the properties and uses of the several refined sulphurs enumerated above it is unfortunate that we do not have a distinctive name for each of the allotropic forms of the element.

Fig. 8. Characteristic Needle Crystals of Brown Monoclinic Sulphur.

For carbon we have the name Diamond to designate the isometric form; Graphite designates the hexagonal form; and Lamp Black designates the amorphous form. To most people however "sulphur is just sulphur" and one form is the same as another. Yet in some important respects the difference in the properties between the rhombic, monoclinic and amorphous sulphurs is just as marked as the well known differences between the isometric, hexagonal and amorphous carbons. One could talk for hours in describing the

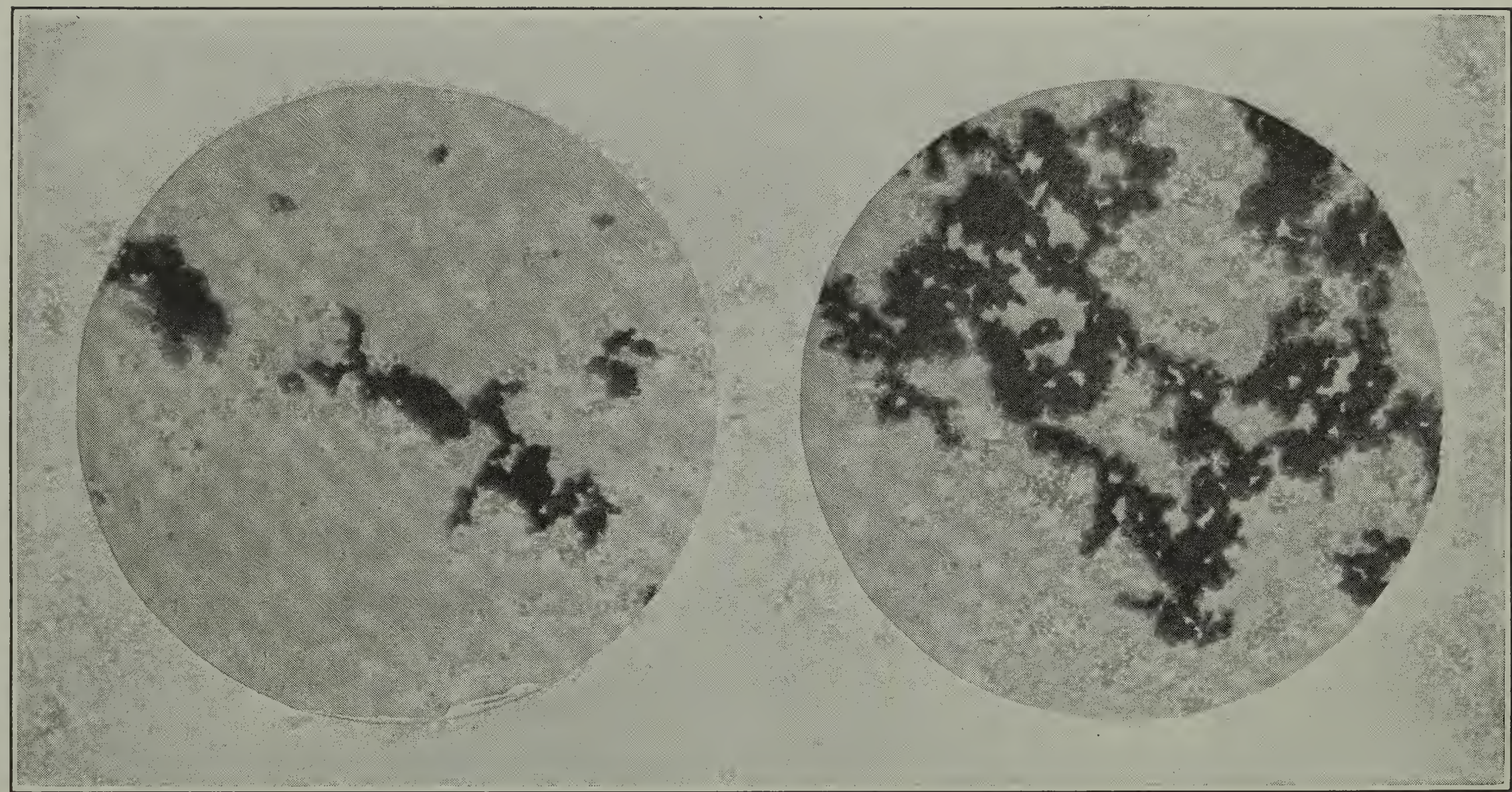
plastic sulphurs; the black, brown, green, blue sulphurs; the soluble forms and many other modifications all very interesting from a scientific point of view.

From the commercial point of view the form of sulphur falling in the monoclinic system is as yet of no importance; though very interesting developments are in sight. Under certain conditions the brownish monoclinic sulphur appears to be quite stable and while in this unusual condition the sulphur may be pulverized to a high degree of fineness without the balling up and sticking during grinding and storage that is a very troublesome characteristic of rhombic sulphur.

As we all learned in our Freshman chemistry the monoclinic form of sulphur under ordinary conditions quickly reverts to the stable rhombic form; this change being accompanied by a reduction in volume and a liberation of heat. Fig. 8 shows the characteristic needle crystals of brown monoclinic sulphur. The needles quickly change color to yellow and at the same time become very brittle going over to the rhombic system though retaining the outward form of the monoclinic crystal. In the figure the reversion is already well under way in the lighter fragments seen in the central part of the print while the darker fragments on the outer part are still distinctly brownish.

The commercially important forms of sulphur are either pure rhombic as in brimstone or a mixture of amorphous and rhombic as in flowers. Fig. 9 shows a photomicrograph of a few particles of ground rhombic sulphur. Unfortunately it is difficult to get a good photograph of sulphur particles. When looking into the microscope however one can easily see the clear sharp fracture faces of each particle which should be compared with the characteristic globular structure of flowers as shown clearly in Fig. 10.

The first commercially important use of sulphur was of course in the manufacture of black gunpowder. For this purpose it is essential that the sulphur be of pure rhombic form as this is the stable form and can be produced absolutely free from acidity. For this purpose sulphur has been refined for centuries. The first refining methods probably consisted in simple liquation processes whereby the moisture and easily volatile impurities were removed. Later on crude subliming methods were undoubtedly used in order to free sulphur from the ore and thus the merits of sublimed sulphur



Figs. 9 and 10. Comparison of Ground Rhombic Sulphur and High-grade Sublimed Flowers of Sulphur. Fig. 9. A few particles of ground rhombic sulphur showing sharp fractures Fig. 10 (same magnification). A single particle of high-grade sublimed flowers of sulphur. Note the agglomeration of a great number of spherical droplets.

became known. Boyle mentions in his "Skeptical Chymist," as noted before, the subliming of sulphur although his remarks do not indicate that sublimation was in commercial use in his times for the manufacture of the two forms of sulphur and the purification of the crude sulphurs.

Molinari states that the first commercial subliming plant was constructed in Marseilles, France, in 1805. In America subliming plants have been in operation on the Pacific coast for nearly half a century; these plants furnishing the rhombic form of sulphur required by the powder mills that were built in the early days to cater to the mining industry of California. A bit later the French and Italian vinyardists that pioneered in the agricultural development of the Golden state required the flowers of sulphur, the merits of which had long been recognized in their home countries. In comparatively recent years the rubber trade is taking an immense tonnage of rhombic sulphur; the principal consumers buying under very rigid specifications as to low content of amorphous sulphur and freedom from acidity and impurities. Thus the demand for refined sulphur is shifting from the Pacific Coast and becoming more and more nation-wide. Eastern agriculturists as yet do not know the merits of high grade sublimed flowers of sulphur so long recognized by their European and Californian co-workers. The sulphur refineries in the East have mainly catered to the trades that use the rhombic sulphurs and only a comparatively small tonnage of flowers is produced, this mainly for the demands of the drug trade.

Sulphur as a Fertilizer and Insecticide

In the notable experiments by Reimer and Powers in Oregon started in 1912 finely pulverized sublimed sulphur was used. In this work these scientists established that the use of this form of sulphur in the soil in quantities from a few pounds up to several hundred pounds per acre would bring about a tremendous increase in many crops. In the practical application of this now famous research the pulverized rhombic sulphur was at first exclusively used, with remarkable success; in some Oregon soils the yield of alfalfa being increased several hundred fold. The yield from the total alfalfa acreage has been doubled by the use of sulphur with only about half of the acreage having yet been treated. In

later years different forms and combinations of sulphur have been tried in soil work with varying results.

I have studied this agricultural use of sulphur from Coast to Coast and can state positively that the addition of proper amounts of sulphur to the soil of very many sections will result in great benefit to the agriculturist, as well as furnish an outlet for an immense tonnage of sulphur. For example, in one section I visited, the average yield of alfalfa cut from some 40,000 acres was slightly less than two tons per acre per year. The addition of sulphur costing the rancher about $1.50 per acre per season would bring the average yield up to over 5 tons of alfalfa per acre per season; at going prices for alfalfa hay this being a net gain of over $30 per acre per season from the $1.50 investment in sulphur.

However this agricultural use of sulphur calls for much more practical study than has been given to date. Sulphur does not always act in the soil as expected. Many conditions, as yet more or less obscure, affect the results. Only careful practical work supported jointly by the sulphur industry and the agricultural interests can bring the benefits that certainly will result for both the consumer and producer of sulphur. To date there has been too much wasted effort in poorly considered investigations as to the uses of agricultural sulphurs. As one distracted County Agent said to me "Newhall, I have shown these farmers what a little sulphur will do for them and I have pled with them to use it; they can afford to, yet they persist in doing as they have always done. It is up to you commercial fellows to help us. I get no support from my Agricultural College superiors as they all seem afraid to commit themselves." I, in due course, talk to the college authorities and find these fine scientists bedeviled by a horde of "commercial fellows" seeking to put something over on the farmer. Where research is being conducted in the colleges on this subject it is mostly "going blind" through lack of practical help from the manufacturing and producing interests engaged in the sulphur industry. Well recognized mistakes known to practical field men are not known to the scientific searchers and vice versa. Thus a lot of money and a world of energy is going to waste and a very desirable and profitable use of sulphur is not flourishing. A notable exception is the work being done at the State Experiment Station in New Jersey; likely equally good work is being done at other Stations but has not yet come to my attention.

The manufacture of insecticides, especially Lime Sulphur, accounts for a large tonnage of powdered sublimed sulphur. This important insecticide and fungicide was at first made almost exclusively from the refined grades of sulphur. In recent years only the small manufacturer and the "home boiler" use refined grades, whereas the large commercial manufacturer uses the crude grades of sulphur. There is a great deal of practical evidence to show that the use of crude sulphur, or perhaps the processes common where this grade is used, give a lime sulphur solution that has properties quite inferior to the solution made from refined sulphurs. There is some scientific evidence also tending to support the practical evidence. The question is now rather controversial because of lack of scientific data. Sufficient to say that lime sulphur solution made from crude sulphur is rapidly falling into disfavor with the practical agriculturist and non-sulphurous substitutes are being used in increasing quantity. One eminent and practical agriculturist advises me privately that he expects that within five years the inroads of substitutes will cut the tonnage of crude sulphur used in the lime sulphur industry squarely in two.

Food Preservation

One of the oldest uses of sublimed sulphurs,—both flowers and rhombic,—is the sulphuring of fruit and other food products. Millions of dollars worth of agricultural products are thus sterilized and preserved in their natural purity. Some of us no doubt remember the hectic controversy of a score of years ago over the so-called bleaching of fruit by the use of sulphur. The use of excessive amounts of improperly refined or even crude sulphurs in early days certainly was open to condemnation. It has now been established that the sulphuring of fruit by modern methods and with high grade sublimed rhombic sulphur or flowers is as healthful a form of sterilization as is the use of heat.

In recent years our ideas of what really constitutes preservation by sulphuring has changed somewhat. We formerly thought that sulphur dioxide was the sole effective agent. Now we have some interesting evidence that sulphur vapor itself or some, as yet obscure, sulphurous compound other than SO_2 also plays an important part. Strange to relate, the burning of crude sulphur, even of 99.5 per cent purity, has been shown under some common con-

ditions to give an entirely different and inferior result than when flowers of sulphur are used under identical conditions. Practical orchardists have long held for the superiority of flowers of sulphur over all other sulphuring agents.

Flowers of Sulphur: Properties and Uses

We now take up the properties and uses of sublimed flowers of sulphur; the most important of all the refined sulphurs. Strictly speaking the term sublimed is a misnomer. Sulphur does sublime rather easily and at temperatures many degrees below its boiling point. There is some evidence that a sublimate is formed even as low as 20 deg. C. The sulphur vapor when in exceedingly minute quantity has an odor much like camphor. At higher concentrations the vapors are very irritating to the nose and eyes, although the nerves soon become deadened to the effects and the discomfort is no longer apparent.

The so-called sublimation process is really a distillation, as the sulphur vapor is superheated well above the boiling point at all times. I have never seen any sulphur crystals on the inner walls of a chamber; although beautiful snow-flake like crystals often form around the kettle and retort housings. The sulphur vapor condenses in the chamber in the form of very minute spherical droplets and not in crystals as is so often stated in the literature. Under the microscope, as noted above, the structure of the flowers is clearly apparent as a mass of these spherical droplets all of uniform size. The highest grade flowers consist of droplets that are free from each other or barely touch. In the heavier flowers the higher temperature in the chamber toward the end of the sublimation period has caused these droplets to coalesce or even fuse together.

I do not know of any research covering the physics of flowers of sulphur. Alexander Smith and his co-workers in the literature previously referred to have shown that the solid sulphur formed when liquid sulphur is suddenly cooled from near the boiling point consists of amorphous sulphur up to about 34.2 per cent together with rhombic sulphur. This is about the same percentage of amorphous sulphur found in the highest grade flowers. Very likely sulphur vapor when it condenses gives exactly the same mixture of rhombic and amorphous sulphur as does liquid on cooling from

a high temperature. According to this research, amorphous sulphur when first formed is liquid even at room temperatures and this liquid state persists for some time. Droplets of amorphous sulphur when observed under the microscope were first liquid; they then solidify, with a later change to monoclinic system although still in the spherical form. Finally the droplets suddenly change from the monoclinic to the stable rhombic system. All this occurs at room temperature. Thus amorphous sulphur is a most unusual substance. It is a sort of coiled spring or a source of potential energy for it should be recalled that each change from the amorphous through the monoclinic to the stable rhombic form is accompanied by the liberation of heat and a reduction of volume.

This unusual property of amorphous sulphur undoubtedly is the reason for the superiority of flowers of sulphur as a sulphuring agent in food sterilization and as a dust insecticide and fungicide, when compared with pulverized rhombic sulphur even tho the particles of the latter are many times smaller than the droplets of the flowers. In making this statement I am fully aware that I am laying myself open to the charge of bringing controversial matter before the members of this Institute for it should be known that in recent years the agriculturist has been very strongly solicited to purchase both crude and refined grades of pulverized sulphur. Molinari and other eminent men have stated that finely pulverized sulphur is superior to flowers in the control of the mildew of the grape. A recent bulletin[8] giving a brilliant piece of research on the toxicity of some sulphur fungicides completely ignores the flowers of sulphur. Yet the tonnage of flowers of sulphur used as a food sulphuring agent and as a dust insecticide and fungicide many times exceeds the tonnage of all other forms of sulphur used for similar purposes. My statement as to the superiority of flowers of sulphur for these uses is borne out by the experience of thousands of practical agriculturists both in Europe and America where powdered sulphur has at all times been obtainable at about the same price as flowers.

Likely the commercial reason for the urge to dispose of powdered grades of sulphur is accountable by the fact that it takes only hun-

[8] "Laboratory Studies of the Toxicity of Some Sulphur Fungicides," by W. L. Doran, Technical Bulletin No. 19, New Hampshire Agricultural Experiment Station, Durham, N. H.

dreds of dollars to set up a grinding plant whereas it takes thousands to produce flowers and sublimed grades. The reason for the difference of opinion among specialists is not quite so easy to explain. I think most likely that opinions have been based on evidence obtained without due knowledge of the very wide range in quality of commercial sulphur of even the same trade designations. For instance I know of one opinion that was based on a comparison between a very inferior powdered sulphur and high grade flowers and another opinion was based on conditions exactly the reverse. Also comparisons have been made under laboratory conditions and in the absence of sunlight which appears to be an essential factor in the effective use of dust sulphur whether flowers or pulverized.

Just what happens when sulphur is used as an insecticide and fungicide is not clearly understood. There is room for a lot of profitable and interesting research. Doran in the paper cited above shows that oxygen is essential under the conditions of his tests and he infers that sulphur dioxide is the lethal agent. On this basis the more powerful action of flowers is explained, for the action of sunlight undoubtedly starts the reversion of the amorphous sulphur. In this change from the amorphous to the rhombic form each droplet of the flowers is shattered by a shrinkage and an immense surface is exposed to the air. At the same time the heat set free by the reversion must promote the union of the sulphur with the oxygen of the air. All practical agriculturists know that sulphur "fumes" best on a bright sunny day.

Powdered sulphur no matter how finely ground could never have the surface that is developed when the droplets of the flowers are shattered by the reversion. There is also much practical evidence to show that the small percentage of "acid" always present in the flowers has an important bearing on the "fuming" properties of flowers. Probably the acid helps start the reversion or helps to preserve the amorphous form till the sunlight unbalances a state of equilibrium that is known to exist between the amorphous sulphur, the rhombic sulphur and SO_2. The acid also undoubtedly has a marked lethal action in itself.

Any one who has worked around a sulphur refinery and suffered from the effects of sulphur vapor will be inclined to attribute a high lethal value to the vapor itself (in spite of the evidence cited above that oxygen is necessary). Very little is known about the

vaporization of sulphur under conditions of sunlight and field temperatures.

There are numerous other uses of the several forms of sulphur that I have not mentioned and one could go on for hours describing the many uses and interesting properties that I have not touched upon. I have brought out the principal points interesting from a technical and commercial point of view. To paraphrase the words of the ancient writer quoted at the beginning of my paper: The virtues of this strange and important element—Sulphur—have scarcely yet been proposed.

PROGRESS IN THE APPLICATION OF CONTINUOUS HYDROMETALLURGICAL METHODS IN THE CHEMICAL INDUSTRY

By JOHN V. N. DORR

Read at the Denver Meeting, July 17, 1924

Introduction

It is now nearly ten years since I read a paper at the Philadelphia meeting of the Institute discussing the application of Dorr methods and apparatus used in hydrometallurgy and chemical fields. At that time they were practically unknown except for the cyaniding of gold and silver ores and in a few places in water recovery from copper ore tailings. It may be of interest to the members to discuss some of the applications that have been made and the difficulties overcome and results obtained since that time. Before doing so, I should like to give a brief resume of the methods and apparatus which are used and some comments on their further development.

The continuous operations with which we have to do are:

1. Sedimentation, or the separation of a dilute or thin suspension of finely divided solids in liquid into clear liquid and a product so thick that often it will barely flow.
2. Classification, or the separation from a suspension of the quick settling particles from the relatively slow settling particles and the bulk of the liquid.
3. Dissolution of a portion of finely divided solid suspended in a solvent or a chemical reaction in which one product is a solid.

Continuous sedimentation is used as a single step where any separation of a portion of a liquid from suspended solids is required both for that purpose alone and as a preliminary to complete separation by filtration.

Counter current decantation or a series of sedimentation operations is also used for complete separation.

Classification is used, directly to make two or more final products, and in closed circuit grinding, wherein the oversize or unfinished product of classification is returned to the grinding medium, it is used to produce a single desired product most efficiently.

Theory of Sedimentation.—Much has been done to determine the laws of sedimentation in the last few years and many theories advanced. At the time I first became interested, metallurgical ideas were that settling capacity was largely a matter of length of overflow weir. We early found that on metallurgical pulp it was largely a function of area while the sanitary engineers felt and still feel and talk entirely of a period of detention. Our present conclusion is that there are a great many factors entering into the question and that it depends largely on the nature of the material to be settled and the density of settled product which is desired. The excellent work of Coe and Clevenger ("Methods for Determining the Capacities of Slime Settling Tanks" given before the Arizona Meeting of the American Institute of Mining Engineers, September, 1916) and the work of Deane ("Settling Problems" presented at the Boston Meeting of the American Electrochemical Society, April, 1920) and others have been most valuable.

The matter has been of the utmost practical importance to us as our work has required us to specify from small scale tests the size and most efficient type of thickeners for a very large variety of problems and conditions. With a stable solid such as a metallurgical pulp the settling rate which determines the rate at which clear liquid can be overflowed is a constant under any given condition so that area is the principal factor, but in settling very dilute suspensions or precipitates formed by coagulation, the rate changes as flocs form and thus time of detention becomes important and largely justifies the position of the sanitary engineers.

Apparatus

Clarification and Sedimentation

The evolution of sedimentation equipment during the past ten years has continued with variations designed to meet different problems presented. The tray thickener has been greatly improved and at present we use two types for most purposes. The open type has one feed, one pulp discharge, with regulated overflow from each tray. The connected type has one feed, but a separate pulp discharge from each tray and the same regulated overflow. This has somewhat greater capacity in many cases. The size of units has increased to 75 feet for tray thickeners and 200 feet for a special design of unit thickener. Settlement of the lightest type of sewage and water purification sludge where current velocity must be

regulated to a low point and other needs brought the development of a thickener or clarifier with extension arms adapted to keep the whole bottom of a square tank clean.

Classification

The principles involved in this work are somewhat more than the mechanical removal of the quick settling particles dropping from a dilute suspension flowing in a settling trough. While in many cases this is true, where dilution of the overflow is five to one or greater, we have found also that the jigging action of the Classifier rakes would allow also a coarse separation at dilutions of 3 to 1 or less, thus making the coarse material act as a jigging bed and throw over the finer sand that would drop out at greater dilutions.

The bowl classifier, which appears a combination of a small, shallow thickener and the usual classifier, has been developed, and can be used to make a separation at 350 mesh on very dilute feeds by virtue of its absolutely quiet pool and large settling area. On the other hand, using a thick feed and emphasizing the jigging action in the rake compartment shown, it has proved able to make a 60-mesh separation with great efficiency.

From the 100-ton classifier of ten years ago we have gone to 1,500-ton units for the large copper properties.

Dissolution

There is not much to be added to what was said ten years ago on this subject. Experience has shown that continuous reactions are feasible and give much closer control over the nature of the precipitate formed than intermittent treatment. The conditions of precipitation, as is well known, affect very greatly the nature of the product precipitated and this has given opportunity for regulation in a way that has made the difference between success and failure in some cases.

Industrial Applications and their Results

Sanitary Engineering

One of the newer uses of Dorr equipment is in connection with sewage disposal and industrial wastes treatment, with the main object of preventing stream pollution, and in water purification.

As both municipal sewage and industrial wastes contain a certain amount of organic solids, which solids by decomposition are the cause of noxious odors and encourage the culture of disease-producing bacteria, the primary feature of all methods of sewage and waste treatment is the removal or oxidization of these solids, part of which are in suspension and part in solution. Those in suspension are in the majority of cases suceptible of settling in a reasonable time, part, however, remain in suspension at any point in the liquid. The means of removing these solids vary from entirely mechanical to a combination of mechanical, gravitational, and induced sedimentation by chemical precipitation. The floating solids consisting in the main of paper, hair, matches, rags, etc., are easily and economically removed by mechanical means such as screens. The solids which will settle may best be removed by gravitational methods, the most common form of unit being a tank or basin of such size or area as to reduce the velocity of the flow of liquid to a point where the solids, in passing through the unit, take a downward course and reach the quiet zone near the bottom before getting close to the discharge side of the tank.

These solids accumulate on the bottom of the tanks in the form of a thick sludge, gradually building up and cutting down the volumetric capacity of the basin, so that after a time the volume is so greatly reduced that solids may actually be picked up and carried along due to the high velocity of flow. To prevent this the simple sedimentation unit is usually built in duplicate to allow of the use of a second tank whilst the first one is being emptied and desludged. The method entails considerable initial expense in constructing the duplicate units, periodical labor charge in removing the sludge, and, as in order to postpone the day of cleaning as long as possible the tanks are usually made deep, this adds considerably also to the initial cost.

It became evident a number of years ago that a shallow unit with some means of removal of the sludge without shutting down the unit or interfering with the continuous flow of sewage would aid materially in reducing the amount of land required, the initial and operating costs of the plant, and would affect the uncertain human element as well as eliminate entirely the need for duplicate units. Some mechanical apparatus for collecting the sludge from the bottom of the tank and removing it would be the most economical and practical solution of the problem.

This idea has led to the development of a tank equipped with a Dorr mechanism, especially adapted for sewage work, and it has been found that such a tank possesses advantages over ordinary sedimentation units.

The Dorr Sewage Clarifier as it is called is so constructed that the sewage or waste water is fed into the clarifier tank at one side, inside a baffle extending below the liquid level. The incoming stream flows horizontally over the entire area of the tank and overflows a weir into a collecting channel at the opposite side of the tank whence it is discharged into sewer or stream. The solids settle to the bottom of the tank, over which, by a combination of flowing and sweeping, they are conveyed to a common point for discharge. The entire area of the bottom of the tank is swept with each revolution of the mechanism. The sludge is withdrawn from the discharge point through the bottom of the tank. The clarifier mechanism operates continuously, but the sludge may be withdrawn at intervals or continuously as conditions demand.

Further benefits became apparent as operation went on, one of the most important being due to the inherent squeezing action of the plows of the Dorr mechanism in reducing the moisture of the sludge. It has been found that Dorr clarifier sludge is lower in moisture than the sludge produced from ordinary tanks. As the disposal of the sludge is the biggest and most difficult problem in sewage treatment, the production of a sludge with low moisture content without expensive dewatering methods means an immediate saving in plant operation costs by having less sludge to handle.

Dorr Sewage Clarifiers have become standard for several methods of sewage treatment—activated sludge, straight sedimentation, direct oxidization, etc., and many of the largest and most representative plants in this country now have them in successful operation.

In the treatment of industrial wastes it is often necessary to remove color, dissolved or colloidal solids as well as large solids, neutralize the effluent, etc., and this usually means a resort to chemical precipitation. As such precipitation produces a more voluminous sludge than ordinary gravitational methods the efficient continuous removal of such sludge is even more essential than in ordinary sedimentation, and in this connection the Dorr Clarifier fits in both efficiently and adequately.

One of the most troublesome features of the ordinary sedimentation tank is based on the tendency of the organic solids to decompose

in a very short time. The product of the decomposition is gas which in rising carries with it particles of solid matter and these form a heavy odorous and unsightly scum on the surface of the tank and introduce an element of uncertainty into the character of the effluent as these gas-buoyed particles are apt to rise close to the effluent side and go out with the effluent. By removing the sludge continuously, this septic action is prevented, scums and odors are eliminated, and the effluent may be depended upon for uniformity of clarification.

For the removal of the larger floating and usually inert solids, mechanical screens have long been recognized as proper units. It is necessary to be able to remove the solids economically and efficiently and most screens require some auxiliary means of removing the screen solids, such as brushes, scrapers, jets of air, or water or suction. The brushed and scraped screens give trouble due to the breaking up of the solids by the brushes and scrapers, with the pushing of the solids through the screen openings. Jetted screens frequently give trouble due to the failure of the jets to remove efficiently the solids, requiring periodical shutdown for hand cleaning.

These troubles encouraged the development of an entirely self-cleansing screen, requiring none of the auxiliary devices. The Dorrco Screen, by reason of its design, direction of rotation of the screen drum, and its speed, efficiently removes from waste water a larger percentage of solids than has been obtained before. It does it without any auxiliary apparatus for cleaning the screen. As there is no abrasion of the screen, plant replacement is eliminated except through breakage or accident. The cleaning of the screen medium is effected by means of a head of water developed on the inside of the screen drum, which water, in its effort to return to its normal level, gushes through the openings in the plate behind the screened solids which have adhered to the outer surface of the plate and washes them into the screen pit. In this pit the solids are picked up by buckets of a self-draining elevator and carried to a convenient elevation for discharging into a receptacle for final disposal.

A similar problem in water softening and purification has been successfully handled with a similar apparatus. The fine flocculent precipitates formed in water softening by the lime soda process or in water purification by treatment with alum or other coagulating

agents are being removed by the clarifier in a number of municipal and industrial plants. Sedimentation to remove the bulk of the suspended solids ahead of sand filtration has been standard practice for many years but it has not been recognized until comparatively recently that means for continuous removal of sludge were justified. When we first investigated the field it was felt that the amount of solids to be handled was so small and the dilution so high that large settling ponds were the only practical units. Experimental work, later substantiated by plant operations, demonstrated that continuous removal of sludge was practical and economical and the Dorr Clarifier, which shows marked savings in initial and operating costs as compared to intermittent units, is now considered by many engineers the standard sedimentation unit for water treatment.

Chemical Processes

The principles of continuous treatment have made rapid progress in the chemical industries and some of the more important applications are as follows:

Alum

In the manufacture of sulphate of alumina or commercial alum the use of continuous agitation for the extraction of the alumina and counter current decantation for washing offers appreciable savings. Four large alum manufacturers are now making use of Dorr Agitators and Thickeners for this purpose by replacing batch solution and settling tanks with continuous equipment. One plant reduced the labor required for these steps from five men to one man per shift and increased the over all yield by more than five per cent. Generally labor costs have been cut in half and the remodeled plant occupies less floor space. The greatest saving, however, is due to lower evaporation costs. Prior to the introduction of continuous leaching and decantation methods in the chemical field most alum manufacturers settled the alum slurry in stationary tanks or boxes. Under these conditions it is impossible to handle slurries above 30° Beaume since stronger liquors tend to crystallize. If combined with wash liquors the solution evaporated usually averaged 25° Be.

By means of continuous hot settling a clear alum liquor of 35° to 38° Be. may be withdrawn from the first Dorr Thickener and sent to evaporation. The steam saving here is very appreciable:

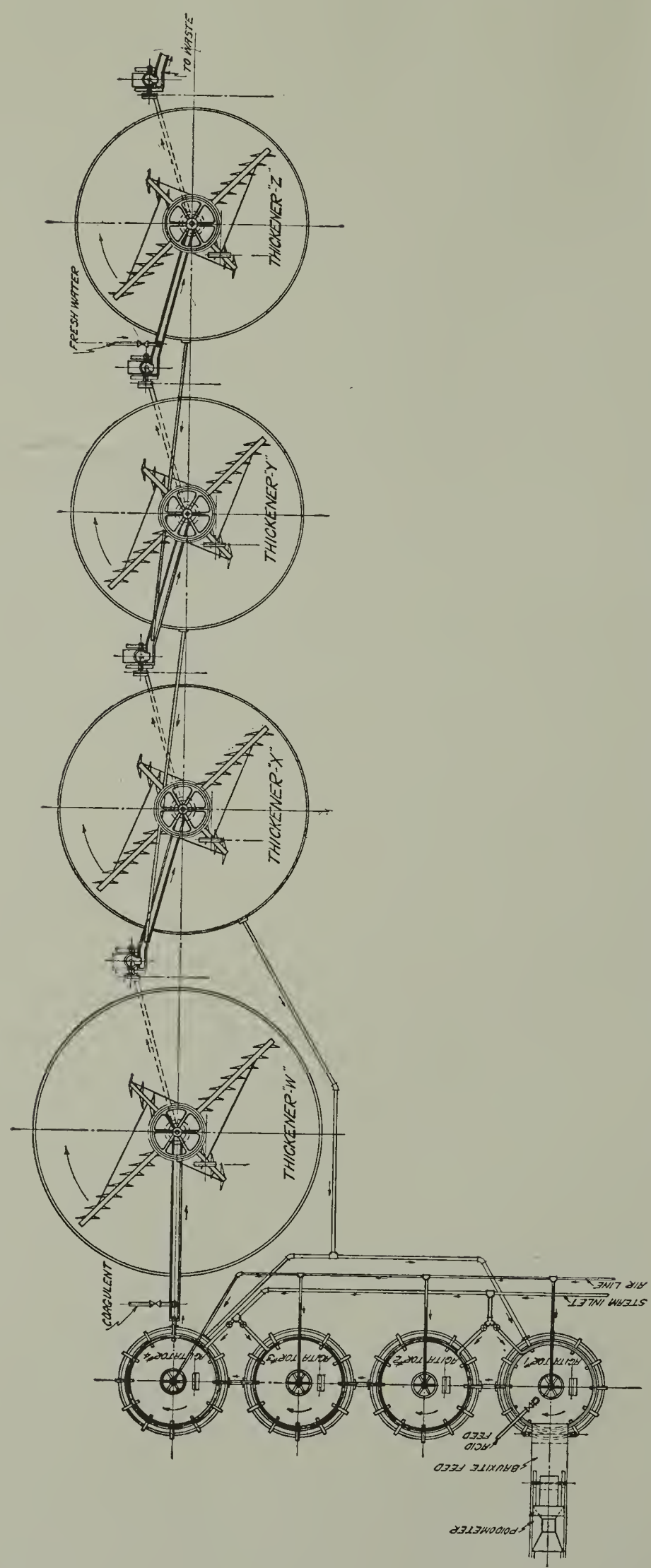


FIG. 1. Arrangement for Continuous Production of Alum

at one plant it was shown to be one dollar per ton of alum produced. It is true that some intermittent plants produce strong liquors and filter these in special presses, but due to filtration difficulties and the corrosive nature of the solution, filter costs, filter repairs, and operating costs are high. In such cases the continuous system shows no saving in evaporation costs, but eliminates or reduces the above mentioned operating costs. Continuous operation in almost every case offers numerous advantages. Raw ingredients entering one end of a plant and waste products and finished material leaving at convenient exits appears to be the ideal arrangement. Not only is the unknown loss reduced in this manner, but the general appearance of the whole system and its cleanliness does much to create an atmosphere which in turn inspires the operators to greater service.

Barium Sulphide and Lithopone

Most of the barium sulphide produced at present is used in the manufacture of lithopone. In general these sulphides are somewhat disagreeable to handle and any labor saving devices are of value in reducing labor turnover. With the general introduction of the continuous kiln for barytes reduction, continuous leaching and washing obviously is advisable. Most American manufacturers have to date adopted the continuous system of settling and washing for barium sulphide. As in alum manufacture continuous hot settling makes possible the production of stronger sulphide liquor and all the other advantages of continuous operation are realized.

Usually the continuous kiln discharges directly into a rotary leaching drum where it is mixed with the weak liquor overflowing the second thickener. The four thickener series replaces the old type percolation tanks and discharges to waste a residue practically free from soluble barium salts. Since the solution flows continuously through all pipe lines, freezing difficulties are reduced or eliminated and an increased yield of a definite quality product is made possible.

Equipment quite similar to the above may also be used for preparation of the zinc sulphate solution for lithopone. For the finished lithopone Dorr installations are in use in various steps of the operation. For dewatering the crude precipitate thickeners are used, for grinding the calcined product bowl classifiers or hydroseparators are in closed circuit with a tube mill; for treating

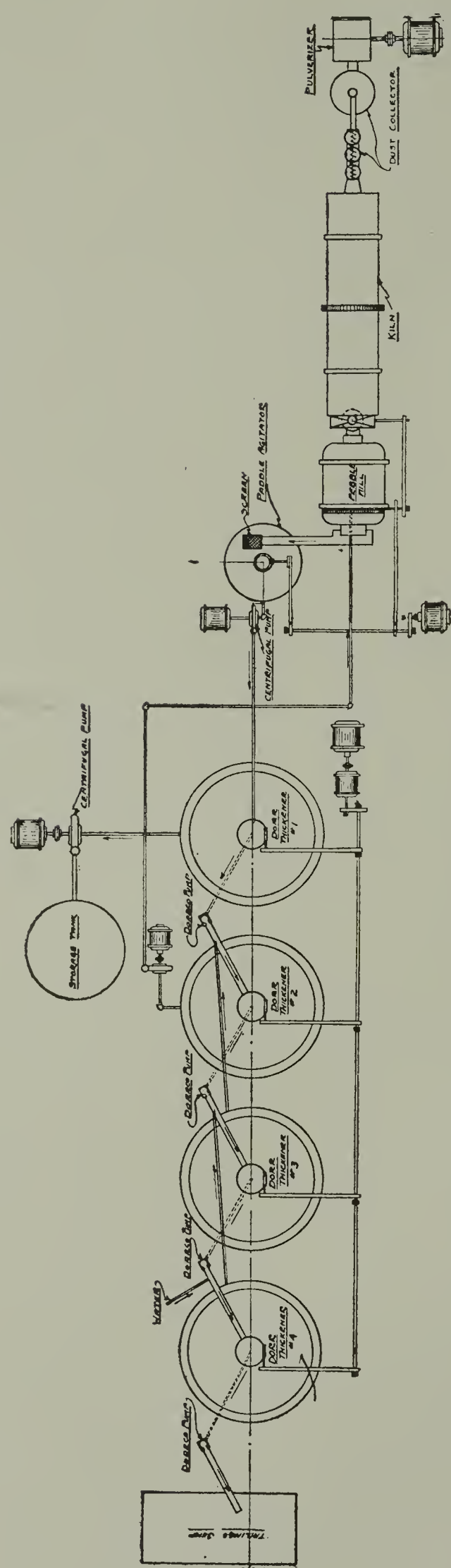


FIG. 2. Layout for Barium Sulphide

and blueing the ground material Dorr Agitators are frequently used whilst the finished product is washed free from soluble salts and dewatered before filtration in a C. C. D. series of thickeners. Due to the size of the lithopone industry and the high dilutions at which the material is handled the continuous method shows very large savings in power, labor, etc. Of more importance than the monetary saving is the superior quality of the finished lithopone

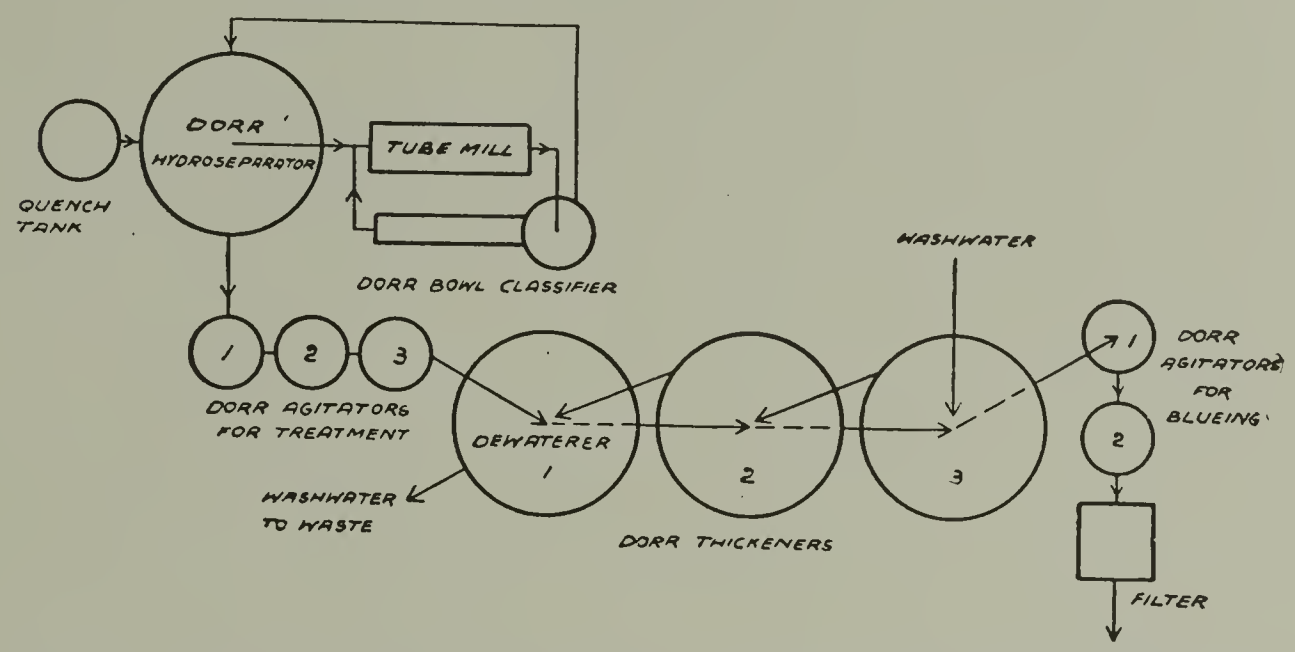


FIG. 3. "Closed Circuit Grinding and Continuous Washing of Lithopone"

produced by the continuous method. Closed circuit grinding in the wet condition seems to produce a texture that can not be duplicated by dry methods whilst the bowl classifier and hydroseparator make possible an extremely satisfactory degree of separation. Continuous operation also insures a uniform product at all times.

Phosphoric Acid

The manufacture of phosphoric acid, superphosphate, and phosphate salts offers an admirable field for the use of continuous digestion and C. C. D. washing. A number of successful installations have been made. Labor requirements have been reduced from two to five men per shift; extraction has been improved 6 per cent to 8 per cent and the washing efficiency and over all yield have improved. Repairs, filter cloth, floor space, etc., are additional arguments in favor of continuous operation.

The production of stronger liquors is again perhaps responsible for the greatest individual saving. Most filtration or intermittent settling plants produced a liquor containing from 12 per cent to

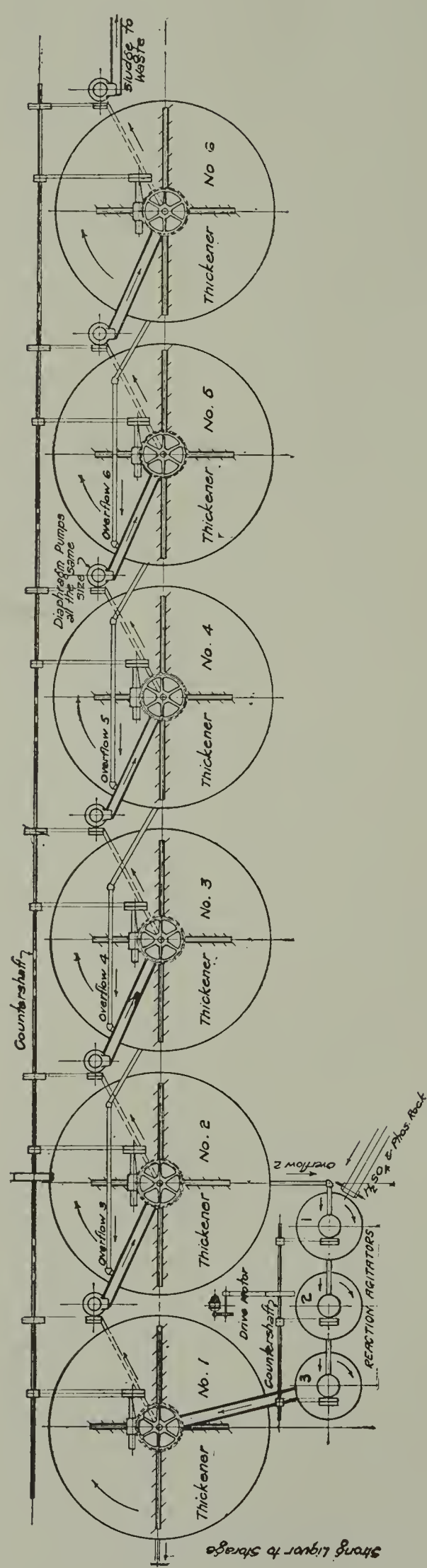


FIG. 4. "Plant for Continuous Production of Phosphoric Acid"

18 per cent P_2O_5 whilst 22 per cent or 30° Be. solutions are easily obtainable with C. C. D. equipment. As these liquors must be evaporated to 50° Be. for superphosphate manufacture this represents a possible $25,000 saving per year for a 40-ton plant. In addition the higher Be. liquor means less calcium sulphate in solution to be gotten rid of during evaporation.

Caustic Soda

To produce caustic soda by the ime-soda ash process it is necessary for economical operation to recover practically all the caustic liquor from the calcium carbonate sludge formed. A C. C. D. series of thickeners has solved this problem satisfactorily. In general the cost of washing the solids in a thickener series is lower than by filtration and in addition filtration of the strong caustic liquor gives rise to other difficulties, materials of constructions, etc.

For a complete continuous caustic plant, a rotary lime slaker in open circuit with a Dorr Classifier is good practice. The classifier removes from the system at once grit and any particles of unburned lime. For the causticizing reaction a series of three agitators serves to give continuous operation and a C. C. D. Thickener series following separates the strong caustic liquor from the carbonate sludge and washes the latter free from soluble salts. The actual conversion varies with the concentration but a 99.5 to 99.9 per cent washing efficiency serves to recover practically all the caustic actually formed.

Again the continuous method saves labor, floor space, initial investment, and gives increase in over all recovery. This layout is satisfactory for small recausticizing operations where it is desired to convert waste carbonate liquor to caustic with little expense and practically no attention. By removing the gritty particles by means of a classifier early in the operation the waste calcium carbonate is of such fineness that it often finds a sale as whiting.

Salt or Crystal Washing

A number of years ago we installed a multi-deck classifier at the plant of one of the large electrolytic caustic manufacturers to receive the underflow from the caustic evaporators. The classifier was fed a dense sludge of sodium chloride in caustic solution and it was desired to remove the last traces of caustic from the salt with a minimum of water. Using but one-third ton of water per

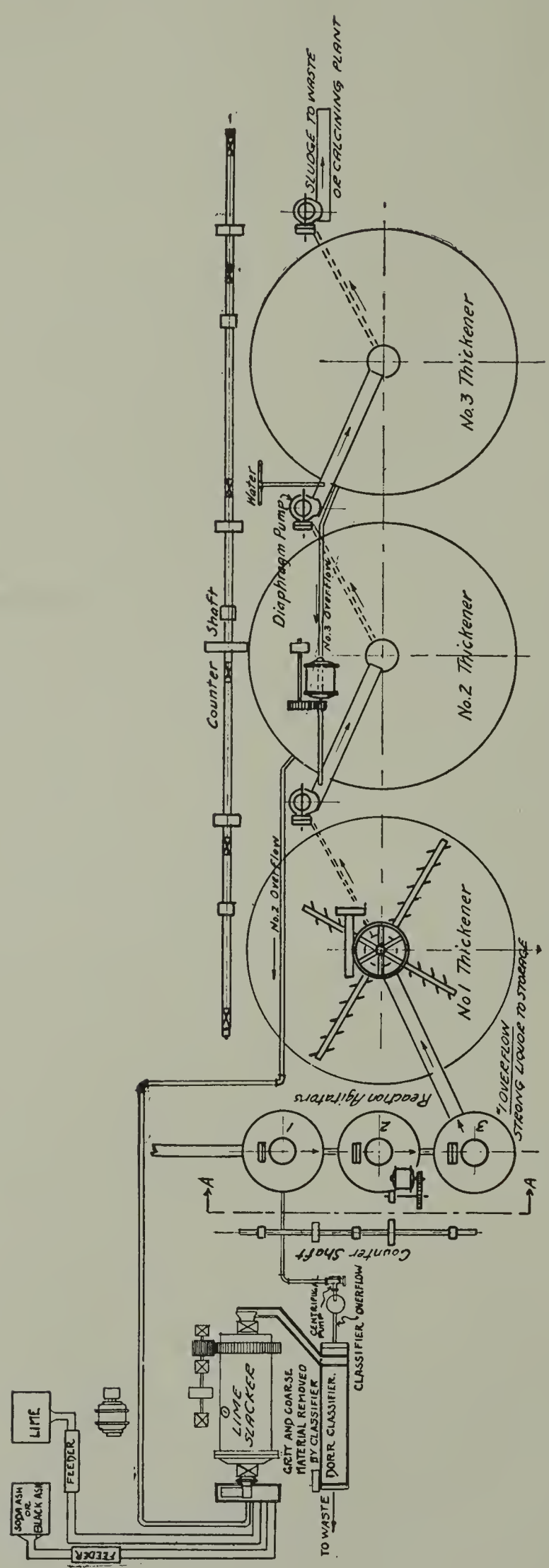


FIG. 5. Arrangement of Caustic Soda Equipment

ton of salt washed, the caustic content of the dry salt was reduced to a few tenths of a per cent. This installation led to others and more recently we have installed other classifiers for removing other crystals from their mother liquors and washing these before centrifuging or drying. In connection with a continuous crystallizer this makes a very satisfactory arrangement but the classifier may as well receive the crystals directly from the base of a continuous evaporator.

Paper

One of the most recent and also most interesting applications of the tray thickener has been in the recovery of white water in the paper industry. The water which passes through the screens carries with it fine fiber and this amount may vary from 2 or 3 lbs. to 12 or 15 lbs. per 1,000 gal. In a large number of plants this fiber goes to waste, the white water being run into a sewer or neighboring stream. This material, if recovered, is a direct saving, as it can be put back on the screens exactly the same as fresh stock. The modified tray thickener or Dorr Save-all, as it is called, has been installed in a number of paper mills with very satisfactory results. It requires practically no attention and usually makes a recovery of 94 per cent to 97 per cent of the fiber. In a moderate-sized plant a saving of from $50 to $75 a day is not uncommon.

Sugar

The production of cane sugar is one of the largest chemical industries, with a total output of 13,000,000 tons. The usual process consists of extracting the juice by passing the cane through a series of rolls in which incidentally a type of "counter current decantation" or washing is used; heating and liming the juice, settling out the mud by intermittent settling tanks and then filtering the same in pressure filter and boiling down the clear juice from the decantation and press.

The rolling, heating and boiling is of course continuous, but the settling is done intermittently in small rectangular tanks called defecators where some final heating is done and where it is necessary to siphon off clear solution from under a layer of foam and floating fibre, with much labor, loss of heat and opportunity by carelessness to get small traces of mud into the boiling house to make trouble in boiling and give an impure sugar.

Although we were told at the beginning that continuous defecation had been tried and abandoned, some large scale experiments were made using a modified tray thickener and now, as the cane sugar juice clarifier, it is regarded as standard by most of the best companies in Cuba and is being installed rapidly.

Its use has resulted in reducing defecation labor one-third and cutting down heat losses and producing a higher extraction of sugar as well as increasing its purity. Many anticipated troubles did not arise and those not expected were readily overcome.

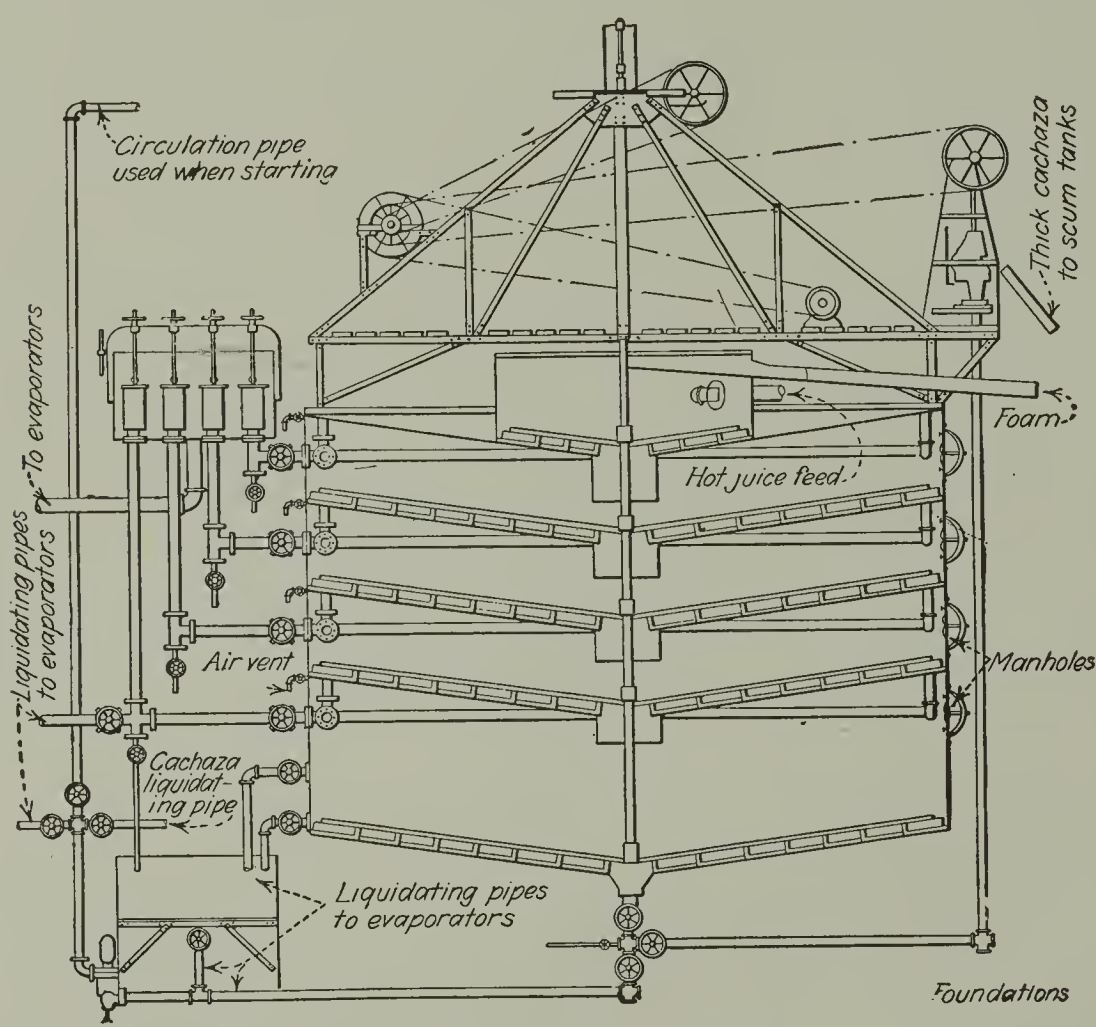


FIG. 6. "Dorr Cane Juice Clarifier'

The machine is heavily insulated so that the drop in temperature of the juice passing through does not exceed 1 per cent or 2 per cent.

As compared with intermittent decantation the mud or settlings is obtained in less than one-half the amount of juice, although the juice itself is much clearer.

In connection with the clarifier the Petree Process, a method of putting back the doubly washed mud upon the stream of bagasse flowing through the rolls instead of filter pressing it, has proved very successful. It does away entirely with the expensive and annoying step of filter pressing the glutinous sticky mud heated

practically to the boiling point and has shown high recovery of sugar as well.

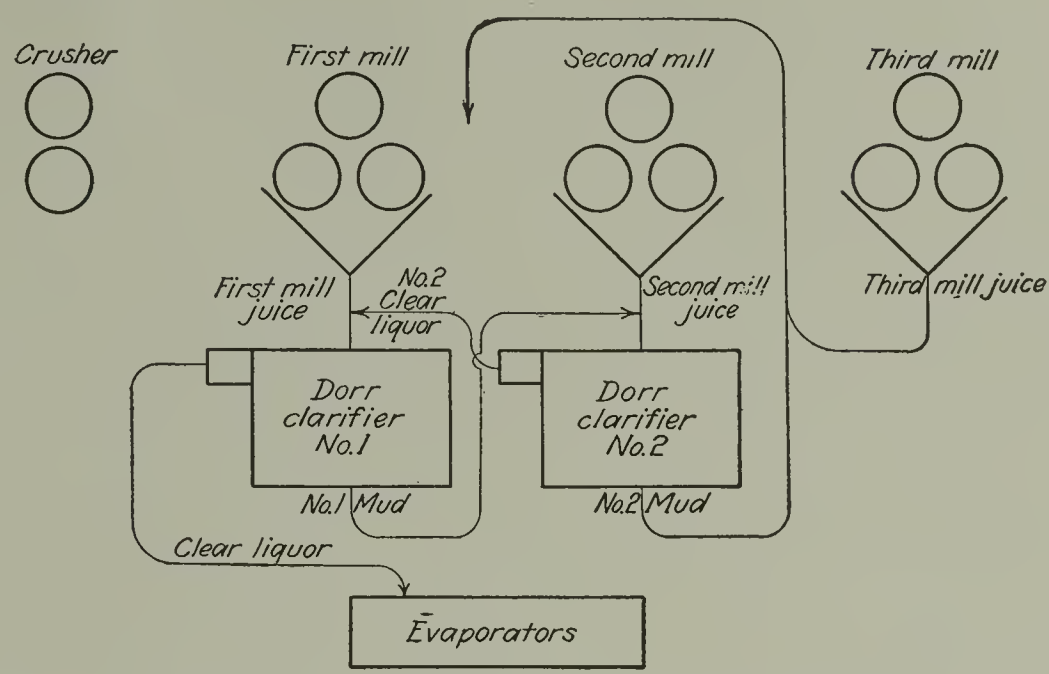


FIG. 7. Typical Petree Process Flow Sheet

In beet sugar factories the thickener has been widely adopted in conjunction with an Oliver Filter to replace the old type of filter press in handling Steffens house precipitate.

CONCLUSION

In addition to the applications described above, Dorr equipment has made for itself a permanent place in the manufacture of alumina, cement and whiting, in the refining of clay and pigments, in the washing of phosphate rock and bauxite, in flue dust and fine coal recovery and in numerous other fields, a description of which is beyond the scope of this paper.

My experience has emphasized the value of studying each industry separately and with an open mind, accepting no methods merely because they "have always been used" and rejecting none on the ground that they "never have been used." It has also demonstrated that different industries can do a great deal to help each other and that methods which have proved sound and lessons that have been learned in one field may be of tremendous value in some entirely different field. Few individuals and few industries or organizations will go far under a policy of isolation and secretiveness, a policy which I am glad to say is rapidly disappearing from engineering circles, and few can fail to benefit greatly by a free and generous interchange of ideas and experiences.

TREATMENT OF INDUSTRIAL WASTES TO PREVENT STREAM POLLUTION

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Sanitary Engineers

The Dorr Company Inc.

Read at the Denver Meeting, July 17, 1924

Industrial or trade wastes may be defined as the liquid discharges or wastes from manufacturing plants or processes and may contain solids incidental to the process. The continued discharge of these wastes into streams has given rise to a serious condition, necessitating drastic action by local, state and federal health authorities to conserve the health and well-being of the people, by requiring the treatment of the wastes as an integral part of the operation of the plant producing them.

Laws governing the discharge of industrial wastes into streams have been placed upon the statute books of nearly every one of the United States and the provinces of Canada, but unfortunately, the means for enforcement, i.e., finances and police power, are not always adequate.

Pollution of streams by industrial wastes may have one or more of the following effects:

Physical pollution, giving personal offence to the individual,

Destruction of fish life,

Contamination of water supplies.

Physical pollution is offence to the eye, nose or skin, and is due to color, odor, turbidity, mud banks, collections of decomposing organic matter or unsightly floating matter. A stream containing such matter is not necessarily detrimental to health, but constitutes an aesthetic nuisance, and is more apt to the suspected than a clear stream.

Destruction or the inhibition of fish life is due to the absorption of the dissolved oxygen from the water by the decomposing organic matter. This supply of oxygen is essential to the life of fish, and in streams or bodies of water where fish are caught for food or sport,

the elimination of industrial waste pollution has come about largely through the efforts of sportsmen. Law suits and fines brought about by owners of cattle or crops damaged by polluted streams also are aids in forcing industrial plants to install plants for the treatment of their wastes.

As many municipalities depend upon the streams passing through, or adjacent to them, for their supplies of water for domestic use, it is essential that this supply be as free from pollution as possible. The presence of industrial wastes makes it necessary for the municipality to install elaborate and expensive filtration plants to render this water safe for human consumption. Owing to the greater expense involved in handling the entire water supply, it is now recognized as logical that the industries should bear the burden of rendering their wastes harmless before discharge into the streams because this can be done at less total cost.

State health agencies have jurisdiction over non-navigable streams within their borders, and those that are navigable are within the scope of the War Department of the U. S. Public Health Service.

In the past, many industrial plants have disregarded this problem, due to the lack of power of enforcement in many states, but public health education has spread to such an extent that the treatment of industrial wastes is becoming well established as a necessary part of plant operation. Many new industrial companies are constructing plants for the treatment of their wastes along with the productive end, so as to be ready to properly treat their wastes from the start.

Characteristics of Industrial Wastes

The wastes from industrial plants vary widely, from day to day, and in some from hour to hour, due to the differing processes used. The variations in color run according to the dye used or the chemical reaction taking place. Wastes from dye manufacturing and textile plants are mostly of bright colors, while from tanneries or other industries, muddy colored wastes are the rule. From some plants the wastes are practically colorless and would appear harmless, but contain large percentages of acids or alkalies and would be a menace to water to be used for human consumption.

Some industrial wastes contain large proportions of solids, others none. The total solids usually have very little significance,

the important factors being the colloidal solids, suspended or organic solids in solution. Wastes from textile mills and dye plants contain little solid matter and the problem is one of color removal or neutralization, whereas wastes from glue factories, tanneries, beet sugar mills, etc., contain very large percentages of solids in suspension and but little color. In the latter instance the removal of the solids is the primary object of treatment.

Scope of Treatment

The type or degree of treatment required for any industrial waste depends upon several things, the most important of which are, size, and the use of the streams used as the recipient of discharge, the proximity of residential districts, bathing places, etc. Where wastes may be discharged directly into municipal sewer systems leading to plants for the treatment of municipal sewage, measures must frequently be taken to eliminate those constituents of the waste which would deposit in the sewers or that would destroy or inhibit the bacteria necessary to the proper functioning of sewage treatment plants.

Another consideration is the volume and strength of the industrial flow as compared to the municipal sewage flow. In many industrial cities, the wastes from the factories equal or exceed the flow of sewage contributed by the population, and where a plant is required to treat the sewage before final discharge, it is manifestly unfair that the municipality should bear the entire burden of treatment. The discharge of caustic and acid liquors into municipal sewers not only is detrimental so the bacterial treatment of the sewage, but it is destructive to the sewers themselves, and these wastes are more economically treated before their entrance to the sewer.

Wastes containing large volumes of readily settleable solid matters cause great expense to cities for cleaning and upkeep. An instance in mind is that of Newark, N. J., where they have a total of over 200 miles of sewers, with one special sewer 2 miles long for a group of tanneries. The expense of keeping this short section clean is one-tenth of the entire yearly sum spent for the upkeep of the system.

Where a number of industrial plants are closely grouped, it is frequently possible to combine their wastes and treat them all in one common plant. This tends to lessen the initial plant cost and

operating cost, which may be apportioned among the users according to the volume contributed.

Methods of Treatment

(*a*) Dilution.
(*b*) Sedimentation, with or without screening or chemical precipitation.
(*c*) Biologic.

The oldest, and until recently, the most used mothed of treatment of industrial wastes was to discharge into the nearest body of water, and depend upon the dilution afforded by the larger volume of water to carry the waste away without nuisance. Due to the growth of municipalities, and their proximity, the increase in the volume of the industrial wastes, and the increasing demand for the use of the streams as sources of water supply, this method is quickly being discarded, except in isolated places. In some cases, however, engineers recognize that where streams cannot be considered as sources of portable water, they may still be used to a certain extent as dilution sources. For instance, the State Health Dept., of Pennsylvania, has set aside certain streams in that state into which industrial wastes may be discharged, inasmuch as these streams can never be recognized as sources of water supply for domestic consumption.

As previously mentioned, certain types of wastes contain solids which may be granular or stringy or fibrous. To illustrate, the wastes from sole leather tanneries contain large percentages of solids which range from animal hairs, small bits of hide, etc., to grit and dirt and lime from the washing and tanning processes.

The stringy, fibrous hide or other large matters may be most readily and economically removed by mechanical means, i.e., by passing the flow through a perforated screen. To prevent deposits on the banks or beds of streams or sewers, floating scums or other nuisances, the removal of the solids in suspension, too fine to be caught by a screen, is best accomplished by sedimentation.

Where solids to be removed are all of a fine nature, or are flocs produced through chemical reactions, sedimentation alone will usually produce the desired result. Sedimentation removes only those solids capable of settling by force of gravity or by chemical precipitation in the time allowed in flowing through the sedimentation unit, as the ordinary sedimentation unit is simply a tank

designed to allow the flow of waste to be slowed down to a velocity that will allow the solids to settle. The size of the tank to allow sufficient reduction in velocity of flow depends upon the character of the solids and the quality of the effluent or overflow desired.

Straight sedimentation, possibly preceded by screening for the coarser solids, may be used only where the effluent from the tank may be discharged without further treatment into streams where ample dilution is afforded. In some cases, screening alone may afford satisfactory treatment, especially if the wastes are to be discharged into tide water or large bodies of water not used for municipal supplies. Where very light, fine or colloidal solids and color are to be removed, it is frequently more economical to resort to chemical precipitation, than to provide the area necessary for straight sedimentation, and in other cases chemical precipitation is absolutely necessary to produce a clear effluent.

In the sedimentation unit the settleable solids form a sludge on the bottom of the unit and must be frequently removed, if a uniformly clarified effluent is to be produced. This removal of sludge may be done periodically and manually, requiring duplicate basins and considerable expense, or continuously by mechanical means. The latter is the most economical method in the average case. Especially where chemical precipitation is resorted to, producing a heavier and more voluminous sludge, continuous mechanical sludge removal becomes the most economical method both to install and operate.

Experience with manually-cleaned tanks, and the recognition of the practical economy of keeping sedimentation units free from sludge, allowing continuous operation and eliminating duplication of units, established the fact that some reliable, simple mechanical means for removing this sludge was desirable. Recognition of this feeling led to the development of the Dorr sewage Clarifier, an adaptation and modification of the Dorr Thickener, for the continuous collection and removal of solids capable of settling.

In the treatment of wastes from practically every class of industrial plant, as well as in municipal sewage and water treatment plants, the Dorr Sewage Clarifier is being extensively and successfully used in all parts of the United States and Canada. Its advantages, aside from the continuous operation of the unit, continuous sludge collection and removal without manual attention, are that it produces a sludge of greater density, giving therefore a

smaller volume to be disposed of; permits the use of shallow units, eliminates the necessity for duplicate units, and assures the discharge at all times of an effluent of uniform clarity, as regards removal of settleable solids. As the sludge is removed before decomposition has begun, there is seldom any scum formation on the surface, and the odors ordinarily experienced in the older type of tanks are obviated.

The operating cost is extremely low, the mechanism being simple, though ruggedly, constructed and slow moving, requiring very little power to run. Manual attention is reduced to the minimum, in the average plant being less than an hour per day.

The Dorr Sewage Clarifier is used for sedimentation units in all types of plants, for preliminary or final settling, following screens, with or without chemical precipitation.

Several year ago the need for a simple, mechanical screen was appreciated and the Dorrco Screen Unit was developed. As this was the first entirely and effectively self-cleansing screen to be marketed, and accomplishing this result without the use of brushes, scrapers, or jets of air or water, or any auxiliary cleaning device, its economy and reliability were soon established and it is now a standard unit in plants where screening is essential. The main features of the Dorrco Screen Unit are its simplicity of construction, making it economical in first cost and operation, the minimizing of wear and the consequent reduction in maintainence cost, the effectiveness of its self-cleansing action, and the fact that it collects and deposits the screenings in receptacles for final disposal without manual attention.

In treatment plants where chemical precipitation is used, it is essential that there be a thorough and effective mixing of the chemicals with the wastes. This is accomplished by the use of a Dorr Agitator which introduces a further element of economy by assuring the complete dissolution of the chemical and by reducing the amount of chemical required. For feeding the chemicals, automatic mechanical feeders are used, which are provided with hoppers sufficient to hold a day's supply of chemical, and requires no manual attention.

Biologic treatment comprises the oxidation of organic solids in suspension and solution. This method is usually carried out in filters of coarse sand or stone. As the rate of filtration is slow, the area required is large and many plants having large volumes of

waste cannot employ this method for this reason alone. Furthermore this method is not applicable to a large number of industrial wastes owing to the inhibiting or retarding effect of constituents of the waste.

It can be appreciated that the treatment of industrial wastes may be carried out by a combination of proven units and methods that reduce the operating cost of the plant to a minimum, cut down the space required for treatment, and produce uniform results. In the average case such a method is not only more economical to employ than biological treatment, but more successful.

The question of initial cost, operating costs, areas required and available, as well as the degree of treatment required must be carefully considered in every case and a thorough study made before the decision as to type of plant is made.

INDEX

PAGE

Acid:
Distillation in silica equipment 101
Nitric:
Concentrating. Experimental apparatus 114
Dilute, concentrating. Babor and Carpenter 111
Distillation 108
Sulphuric, Distillation 106
Activation of waste 49
Agitator, for alum industry. Dorr 191
Air pockets, location of in jacketed apparatus 97
Alfalfa, use of sulphur on, ground 177
Alcohol from beet molasses 35
Alkalinity, of treated boiler water 157
Allotropes, of sulphur 173
Alumina, manufacture of 201
Aluminum pans, heat transfer in 89
Anderson, Evald:
Some factors and principles involved in the separation and collection of dust, mist and fume from gases 69
Apparatus, chemical, heat transfer calculations 87
Arsenic in sulphur 172
Asbestos rope, used in silica still construction 101
Shredded magnesia, insulation 103
Asphaltic matter in sulphur 172
Atmosphere, pollution of 69
Alum:
Evaporation of, solution 191
Filtration of 193
Manufacture of 191
Used in water treatment 154
Aluminum Sulphate, removal from water 149
Babor, Joseph A. and Carpenter, Clifford D.:
Concentrating dilute nitric acid 111
Bachmann, Frank, and Besselievre, E. B.:
Treatment of industrial wastes to prevent stream pollution 203
Barium:
Carbonate:
Cost of 38
Oxide, by De Guide process 38
By Italian process 41

PAGE

Barium Process:
Of desugarizing beet molasses. Dahlberg 35
Decline of process in France 37
Developed by Dubrunfaut and Leplay 37
Development in Italy 40
Economics involved 38
Italian practice described 42
Flowsheet 43
Necessary considerations in applying in the U. S. 43
Poisoning from bi-carbonates 44
Sulphide:
Manufacture 193
Continuous washing of 193
Barr, William M.:
Chemical engineering aspects of water treatment for railroads 149
Bartow, Edward:
Disposal of waste from beet sugar industry 47
Barytes, reduction of 193
Bauxite washing 201
Beater mills, for grinding sulphur 172
Beet Sugar:
Analysis of beets 57
Cost of recovering last traces from molasses 26
Cold saccharate process. Filters 13
General description 20
Filtration problems. Maudru 1
Fuel consumption 64
Hot saccharate process. Shafor 19
Economics involved 26
Control of temperature in 26
Precipitate, composition of 25
Relation to Steffens process 19
Temperature-precipitation curve 21
Use of lime in 24
Industry. Disposal of waste from. Bartow 47
Labor requirement for production reduced 66
Molasses:
Barium process of de-sugarizing. Dahlberg 35
Precipitation of sugar from hot saccharate solution 21
Pulp, waste water from 47
Slicing capacity and extraction records 62
Wastes, heated, temperature versus sugar concentration 22
Available CaO versus sugar precipitated 23
Berl, apparatus for studying nitric acid concentration 114
Besselievre, E. B., and Bachmann, Frank:
Treatment of industrial wastes to prevent stream pollution 203
Bicarbonates, cause foaming of boiler water 151

PAGE

Bocters, on water binders 112
Booth, on treating water 153
Bowl classifier 187
Boyce, on nitric acid 111
Calcium:
Chloride solution, as bath liquor 116
Oxide, see under lime.
Salts, removal from water 149
Sulphate, elimination in phosphate manufacture 197
Tri-suchrate. Steffen process 13
Calder-Fox scrubber 79
Calorimeter, for steam measurement 91
Carpenter, Clifford D., and Babor, Joseph A.:
Concentrating dilute nitric acid 111
Carbonates in boiler water 150
Carbonation, beet sugar liquors 2
Castor oil, anti-foam agent 151
Caustic Soda, manufacture of 197
Cement, size of particles 70
Chambers, for sulphur refining 170
Chemical Engineering aspects of water treatment for railroads. William M. Barr 149
Chromel wire, for heating silica still 109
Clarification:
Apparatus for 186
Of sewage 189
Clarifier, sewage 208
Classification, definition of 185
Classifier, bowl 187
Clay, refining 201
Clevenger, on slime settling tanks 186
Coagulation of precipitates 186
Coe on slime settling tanks 186
Coke, used to reclaim $BaCO_3$ 42
Collection of solids separated from gases 72
Colloidal solids in wastes 189
Condensers:
For sulphur sublimer 165
On nitric acid stills 116
Silica 101
Convection current velocity, factor in heat transfer 89
Copper pans, heat transfer in 89
Corrosion:
Of locomotive boiler tubes 151
Photographs of, of boiler tubes 158
Sulphur containers 171
Water softening tanks, allowing for 156

PAGE

Cost accounting—importance of daily operating reports 57
Cottrell, on nitric acid 111
Creighton, on nitric acid 111
Crushing and grinding:
In connection with classification 185
Lithopone 193
Makes necessary dust collection 69
Of sulphur 172
Raymond mill for lime 36
Crystal Washing 197
Crystallization:
Fractional, of nitric acid 115
Von Veimarn's law 27
Crystallizer, continuous 199
Cyaniding, gold and silver ores 185
Cyclones, for dust collecting 73
Dahlberg, H. W.:
Barium process of de-sugarizing beet molasses 35
Discussion:
Dr. John C. Olsen 44
Mr. Bailar 44
Prof. Alfred H. White 44
Dr. A. N. Bennett 45
Deane, on settling problems 186
Decantation, counter current 185
Decomposition of organic matter in industrial wastes 190
Defecators, in sugar industry 199
Continuous 200
De Guide process for forming BaO 38
Commercial difficulties anticipated 40
Density, liquid, factor in heat transfer 89
Dessau sugar refinery, Germany 37
De-sugarizing beet molasses. Dahlberg 35
Disposal of waste from beet sugar industry. Edward Bartow 47
Dissolution 185
Distillation:
Acid, in silica still 101
Flask, for studying nitric concentration 114
Fractional, in producing nitric acid 111
Methods for nitric acid 112
Nitric acid-water system. Data 119
Nitric-sulphuric mixtures:
Data 140
Equations for 145
Model showing relations 144
Procedure 117
Ternary plot showing behaviour 146

PAGE

Distillation, pyrex for 116
Rate of, of nitric acid 147
Sulphuric, nitric, water mixtures 143
To insure passable water for boilers 150
Versus sublimation, of sulphur 180
Dorr Equipment 185
Dorr, John V. N.:
Progress in the application of continuous hydrometallurgical methods in the chemical industry 185
Dowell, M. H., Olin, H. L., and Toynbee, C. M.:
Heat transfer in steam jacketed kettles 87
Drier, spray, on Steffen's waste 52
Dust:
Cement, separation from alkali dust 71
Density. Influence on settling 74
Effect of difference in particle size on behaviour 71
Mathematical treatment of settling data 76
Metallurgical. Settling studies of 75
Particle size measurement 70
Separation from gases 69
Settling:
Calder-Fox apparatus 79
Chamber. Construction of 75
Stokes law 75
Surface characteristics of particles 71
Zinc, particle size 71
Dye plants, wastes from 204
Electric:
Agglomeration to effect dust removal 83
Importance of 83
Furnaces, for converting barium carbonate to oxide 40
Description 41
Heating unit for silica still 101
Precipitation to remove dust 83
Limitations of 83
Mechanism of 83
Silica still, Tyler 101
Thermal efficiency 104
Enamel lined pans, heat transfer in 89
Evaporators:
Enamel lined, heat transfer coefficients 96
Heat transfer in steam jacketed. Olin, Dowell and Toynbee 87
Lowering, costs in alum industry 191
Nitric acid 111
Open pans, heat transfer in 89
Quintuple, cleaning effects singly 63
Steam jacketed, air pockets in, location of 97

PAGE

Evaporators, vacuum 89
Explosives, sulphur for 167
Fans for dust collecting 73
Fertilizer from beet sugar wastes 52
Films, importance of composition of, in heat transfer studies 88
Filters:
See also thickeners.
American, for cold saccharate 15
Description of 15
Beet sugar carbonation, Comparison 12
Carbonation, in beet sugar plants 1
Cloth. Relative costs 16
Life in hot saccharate process 26
Cold saccharate 13
Excelsior in water treatment 155
Factors influencing selection of 3
Haubold 16
In connection with sedimentation 185
Kelley, for beet sugar industry 3
Plate and frame, for beet sugar industry 2, 14
Losses on, cold saccharate process 14
Rotary vacuum drum types for cold saccharate 15
Sand, maintenance of 155
Solids from gases 73
Sweetland:
Description of 6
Comparison with other types 6
Vacuum, in connection with thickener in beet sugar industry 6
Vallez 5
Difficulties in use of 5
Use on hot saccharate 5
In hot saccharate process 26
Filtration:
Beet sugar, problems 1
Boiler water treatment 155
Carbonated sugar liquor, Cost of 12
In cane sugar manufacture 199
Of alum liquors 193
Of $BaCO_3$ precipitate 42
Of phosphoric acid 195
Of polluted stream water 204
Waste beet sugar liquors 48
Fish life, effect of waste on 203
Foam:
Formation in hot saccharate process 27
Troubles in handling cold saccharate 15

PAGE

Foaming:
Castor oil to eliminate 151
Of boiler water 150
Food preservation, with sulphur 179
Fractionation, see also **distillation:**
Of heavy acids in distillation 123
Frischer, on water binders 112
Fuel consumption in beet sugar plants 64
Fumes:
Agglomeration of, particles 71
Separation from gases 69
Settling of, in ordinary apparatus 75
Stoke's law 75
Fungicide, sulphur as 173, 182
Furnace draft, increased, makes necessary dust collection 69
Gas and gases:
Despersoids 69
Nature of 70
Influence of charges carried 72
Agglomeration through 72
Ions formed in 72
Non-condensible, in steam jacketed equipment 97
Separation of mist, fume and dust from 69
Velocity of. Importance in design of dust settling chambers 77
Viscosity, effect on particle settling 74
Glass, conductivity of in heat transfer calculations 97
Glue factories, waste from 205
Glycerine, for elevating b. p. 116
Grinding, see crushing.
Gunpowder, use of sulphur in 175
Guttman on sulphur sublimers 164, 165
Hardness, of water, removal of 149
Elimination. Limits of 157
Hazard, static, in sulphur refining 170
Heat:
Balance on silica still 109
By means of steam jackets 89
Efficient utilization in beet sugar plants 65
Electrically produced 109
Transfer:
In steam-jacketed evaporators. H. L. Olin, M. H. Dowell, and C. M. Toynbee 87
By conduction, factors underlying 89
Cleanliness factor 97
Direct measurement of coefficient for 87
Errors in calculation of 98
Film coefficients 96

PAGE

Heat transfer, formula for overall coefficient. McAdams and Frost 87
Overall coefficients, test 89, 94
Summary of factors affecting 98
Test kettle construction 90
Hoover, C. P., on treating water 153
Hot saccharate process of the beet sugar industry. R. W. Shafor 19
Apparatus used 31
Precipitate, variation in 28
Dilution to make uniform 29
Recovery. Purity of product 32
Howard dust catcher 72
Hydrogen ion concentration in feed water 151
Hydrometallurgical methods, application in the chemical industry 185
Hydrostatic head, factor in heat transfer 89
Industrial wastes, disposal of 189
Injectors, coating of 150
Insecticide, sulphur as 173
Insulation:
Of continuous defecators 200
Of silica still 102
Ionization of gas in electrical precipitators 84
Ions, in water versus gas 72
Iron pans, heat transfer in 89
Kelley filter, description of 3
Operation; pressure control 4
Washing cake on leaves 4
Tests for cake thickness 4
Use in connection with rotary vacuum 8
Kettle, for heat transfer studies 90
Kieselguhr, use with carbonated beet sugar liquors 5
Kiln, continuous for barytes reduction 193
Küster, production of pure nitric acid 115
Leaching, Continuous 191
Lead lined pans, heat transfer in 89
Lime:
In caustic soda production 197
In cold sugar waste, versus sugar precipitated 23
Behaviour in hot and cold processes 24
Soda treatment of water 154
Sulphur, insecticide 178
Use in beet sugar industry 12, 48
Lindenthal, W., Olsen, J. C., and Sherman, I.:
Tyler electric silica still 101
Thermal efficiency 104
Lithopone manufacture 193
Locomotive boilers, water for 149
Lunge. Sulphur, discussion of 165

PAGE

Magnesia asbestos insulation 103
Magnesium salts, removal from water 149
Maudru, Joseph:
Filtration in the beet sugar industry 1
Discussion:
William C. Brainbridge 16
Richard D. Moore 16
Phillip H. Groggins 16
Crosby Field 16
Metals, in apparatus construction 90
Mist:
Separation from gases 69
Settling of. Stokes law 75
Mixing and agitation:
Essential in dilution of cold saccharate waste 29
In water treatment 153
Molasses:
Annual production of 36
Beet, composition of 35
Uses for 35
Waste, utilization of 49
German practice 51
Patents on 50
Possible uses for 50
Source of many compounds 50
Molinari. Sulphur refining 164
Monel cloth for Vallez filters 5
Münch, production of pure nitric acid 115
Newark, trade waste problems of 205
Newhall, Charles A. Refined sulphurs: their manufacture and uses 163
Nitric Acid:
Concentrating dilute. Babor and Carpenter 111
Apparatus for study of 114
Decomposition of 116
Distillation in silica equipment 108
Cost of 109
Effect of water on 116
Equilibrium with sulphuric and water. Mathematical treatment 138
Data on 126–136
Fractional crystallization of 115
Fuming for making test solutions 115
Liquid-vapor equilibrium 121
Literature, review of 111, 148
Oxides in 115
In distillate 120
Patents covering concentration 113
Potassium acid sulphate in distillation of 112

PAGE

Nitric Acid, preconcentration 112
Production of 111, 115
Pure, method of Küster and Münch 115
Superconcentration 112
Synthetic, arc. Concentration 113
Nitro cotton spent acid concentration 113
Nitrogen oxides, in nitric acid 115
Nitroglycerine, effect on demand for nitric acid 111
Spent acid concentration 113
Nitrous acid, in nitric 115
Northern Sugar Corp.'s problems in waste disposal 51
Solution 52
Olin, H. L., Dowell, M. H., and Toynbee, C. M.:
Heat transfer in steam jacketed kettles 87
Odor, of waste, elimination 190
Olsen, J. C., Lindenthal, W., and Sherman, I.:
Tyler electric silica still 101
Thermal efficiency 104
Organic waste disposal 47
Oxide film in heat transfer studies 97
Oxygen, elimination from water 151
Packing for silica acid still 106
Paper and pulp:
White water recovery 199
Pascal, apparatus for studying nitric acid concentration 114
Pauling. Equipment for nitric acid concentration 113
Peligot's discovery of barium mono-saccharate 37
Phosphate rock, washing 201
Phosphoric acid, manufacture of 195
Pigments, manufacture 201
Pollution:
Of atmosphere 69
Physical, defined 203
Stream, prevention of 203
Polysulphides, sulphur from 173
Ponds, use of for treating beet sugar waste liquors 52
Poste, on enamel lined equipment heat transfer 96
Potassium acid sulphate, use in nitric acid distillation 112
Power cost, silica still 104
Precipitator, electrical 84
Precipitation:
Of solids in industrial waste 189
Of suspended matter in waste 207
Progress in the application of continuous hydrometallurgical methods in the chemical industry. John V. N. Dorr 185
Pyrex, for acid distillation 116
Radiation, factor in heat transfer 90

PAGE

Refined sulphurs: their manufacture and uses. Charles A. Newhall 163
Refinery, sulphur 168
Retort, sulphur 165
Rubber, use of sulphur in 177
Saccharate:
Difference in alkaline earth 36
Hot, solutions, Vallez filter for 5
Tri-calcium 20
Tetra-calcium 20
Salt washing 197
Samtleben, apparatus for studying acid concentration 114
Saveall, Dorr, for white water 199
Scale, salts that form, removal of 150
Screens:
Dorrco, description of 190, 208
For handling industrial waste 190
Screening, impurities from waste sugar water 47
Sedimentation:
Apparatus 186
Definition 185
In sewage disposal 187
In water treatment 155
Of trade wastes 206
Theory of 186
Separation:
And collection of solids from gases, apparatus 72
Filtration methods 73
Influence of medium 81
Necessity for cleaning apparatus 82
Temperature and humidity factors 82
Inertial methods 73, 78
Critical velocity 79
Design of apparatus 80
Limitations of 79
Mathematical treatment 78
Stokes law 78
Sewage:
Clarifier 208
Cost of treatment of 209
Disposal 187
Shafor, R. W.:
Hot saccharate process of beet sugar industry 19
Discussion:
Mr. Baird 32
Sherman, I., Olsen, J. C., and Lindenthal, W.:
Tyler electric silica still 101
Thermal efficiency 104

PAGE

Silica still, Tyler electric 101
Thermal efficiency 104
Sil-o-cel, used as kettle lagging 91
Skimming, sulphur 170
Slime settling 186
Sludge, sewage, disposal of 187
Smith, Alexander:
Work on sulphur 171
Smoke, oil, Charge of particles 72
Sodium:
Aluminate as a water softener 160
Chloride, washing 197
Hydroxide, manufacture of 197
Nitrate as intermediate in nitric acid making 112
Silicate, used with asbestos in silica still sealing 103
Softeners:
For water, factors in selection of 153
Sodium aluminate as a 160
Zeolite as a 160
Softening Apparatus:
Cooper Lake, Wyoming 154
Council Bluffs plant 152
Junction City, Kansas 156
Las Vegas, Nevada, plant 155
Shape of 154
Soil, effect of sulphur on 178
Some factors and principles involved in the separation and collection of dust, mist and fume from gases. Anderson 69
Spattering in stills, study of 110
Static, in sulphur refining 170
Steam:
For hot saccharate process 28
In direct nitric concentration 113
Jacket heating 89
Air pockets in 97
Steffens Process:
Compared to barium and strontium processes 36
Description 13
Flowsheet 19
History of 36
Waste disposal 49
Sterilizing, using sulphur 179
Stills:
See also distillation.
Test of silica, method and data 105
Tyler electric silica 101
Spattering in 109
Thermal efficiency 104

PAGE

Stokes law of settling 73
Strontium for desugarizing beet molasses 36
Process:
Used in Germany 37
Discussion of 37
Sublimers for sulphur 165, 170
Sugar, see also **Beet sugar:**
Cane:
Bagasse 200
Liming juice 199
Petree process 200
Production of 199
Rolling 199
From molasses. Steffen process 13
Industry. Technical accounting in. Zitkowski 55
Comparisons of operating costs 56
Results obtained 64
Sample record sheets 58
Sulphates, removal from boiler water 149
Sulphur:
Refined, manufacture and use. Newhall 163
Acid elimination 170
Agricultural uses of 177
Annual consumption of 163
Arsenic content of 172
Crude versus refined 182
Dioxide, in refining chambers 171
Flowers 172
For agricultural purposes 171
For explosives 167
For rubber industry 177
From polysulphides 173
Grades of 172
Gravitational methods 72
In food preservation 179
In gunpowder 175
Italian, refining 170
Japanese, refining 170
Magister 173
Moisture removal 173
Monoclinic 173
Odor of 180
Precipitated 173
Refineries 163, 173
Rhombic 175, 181
Skimming 170
Smith, Alexander, work of 171

PAGE

Sulphur, spraying method 73
Sublimers 165
Sulphuring fruit 179
Sulphuric Acid:
Amount required to distill nitric 145
As water binder 112
Equilibrium with vapor in presence of nitric 125
For experimental purposes 116
For making nitric acid 111
Mist, removal of 79
Quality of product distilled in silica equipment 107
Cost of distillation 108
Silica still for, construction 106
Superphosphate, manufacture of 195
Suspended matter, see under gas dispersoids.
Tank for precipitation of solids from hot saccharate solution 30
Waste, character of 204, 206
Tar, separation from gas 72
Technical accounting in the sugar industry. Zitkowski 55
Temperature:
As factor in water treatment 153
Control, rigid, essential in hot saccharate process 26
Gradient, in heat transfer 89
Effect of 93
Variation in, of jacketed apparatus 97
Ternary acid system studies 114
Textile plants, waste from 204
Tetra-calcium saccharate 20
Thermal syndicate still 101
Efficiency 104
Thickeners:
Caustic soda production 197
Continuous, in sugar industry 200
Dorr, in beet sugar industry 6
Description of 6
Difficulties incident to operation 7
In hot saccharate process 26
For various pulps 186
Genter 11
Sketch of 10
Capacity of 11
Oliver-Burden 8
Capacity 9
Description of 9
Phosphoric acid production 196
Tray types 186
Trinitrotoluene spent acid, concentration 113

PAGE

Towers, for nitric concentration 113
Toynbee, C. M., Dowell, M. H., and Olin, H. L.:
Heat transfer in steam jacketed kettles 87
Tube mill, used with classifier 193
Tyler electric silica still. Olsen et al. 101
Thermal efficiency 104
Unit processes, importance of heat transfer in 87
Veley, on dissociation of nitric acid 116
Viscosity:
Factor in heat transfer 89
Of gas, effect on settling of particles 74
Volatilization, complete, makes necessary fume collection 69
Von Veimarn's law of crystallization 27
Waste:
From beet sugar industry, disposal of. Bartow 47
Magnitude of 47
Sources of:
Beet washing water 47
Battery water 47
Lime sludge water 49
Steffens waste 49
Use as fertilizer 52
Beet sugar 205
Biological treatment of 208
Caustic as a trade 205
Industrial:
Characteristics of 204
Clarification of liquids 189
Definition 203
Methods of treatment 206
Yeast treatment 49
Activation 49
Lime treatment 49
Prevention of stream pollution by 203
Sugar:
Holland-St. Louis experiments at Decatur plant 48
Lime, used as precipitant 48
Washers for dust collection 73
Washing, salts and crystals 197
Water:
Treatment for railroads. Barr 149
Binders, discussion of 112
Contamination of, by trade waste 203
Distilled, for evaporator experiments 92
Softeners, construction of 152
Softening:
Use of continuous clarifier 191

PAGE

Treatment:
Agitation required 153
Alum, use of 154
Cost of 160
Factors entering 149
Lime soda 154
Over. Results of 150
Sludge handling 154
With sodium aluminate 160
Zeolite for 160
White water recovery 199
Whiting, manufacture of 201
Yeast:
Manufacture using beet molasses 35
Treatment of waste 49
Zeisberg:
Equipment for nitric acid distillation 112
Zeolite water softener 160
Zinc sulphate, manufacture of 193
Zitkowski, H. E.:
Technical accounting in the sugar industry 55
Discussion:
Pres. Reese 66
Prof. Alfred H. White 66

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